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Formation of Magmatic Nickel Sulfide Ore Deposits and Processes Affecting Their Copper and Platinum Group Element Contents

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Abstract

Nickel-copper sulfide ore deposits are found at the base of mafic and ultramafic bodies. All their host rocks, except the Sudbury Igneous Complex, are thought to be mantle-derived melts. The Sudbury Igneous Complex is thought to be the product of complete melting of continental crust.

In the case of mantle-derived magmas, a high degree of partial melting of the mantle serves to enrich the silicate magma in Ni and platinum group elements (PGE). This magma must then be transported to the crust by an efficient process in order to reduce the possibility that Ni is removed from the magma by crystallization of olivine. Once the magma is emplaced into the crust, S from some source must be added to bring about saturation of the base metal sulfide liquid. An ideal site for all of these processes is where a mantle plume intersects a continental rift. The plume provides a large volume of magma, produced by a high degree of partial melting. The normal faults of the rift provide easy access to the crust so that the magma is transported efficiently. In many cases rifts contain sedimentary rocks rich in S, thus providing an ideal source of S for sulfide saturation. The heat from the plume can lead to melting of a large volume of rift sediments and release of S from the sediments to the Ni-PGE–rich primary magma. In the case of the Sudbury Igneous Complex, a very large volume of superheated magma formed by flash melting of the crust. This melting event was the result of the impact of shock waves from the explosion of a large meteor in the atmosphere.

In both the case of mantle-derived magma and the case of the Sudbury Igneous Complex, once sulfide liquid formed as suspended droplets in the silicate magma it must have interacted with a large volume of mafic magma in order to become enriched in Ni, Cu, and PGE in the sulfide. This enrichment occurred when the droplets were transported or when they were suspended in eddies. The magma from which the Sudbury Igneous Complex formed was superheated and base metal sulfide liquid formed at approximately 200°C above the magma liquidus. Thus the Sudbury sulfide liquid had more time to equilibrate with the silicate magma than a sulfide droplet in a mantle-derived magma. This extra time and the huge volume of silicate magma in the melt sheet allowed the sulfide liquid to maximize the concentration of Ni, Cu, and PGE. The efficiency of the metal collection step in the case of the Sudbury Igneous Complex counterbalanced the fact that this crustal-derived magma had lower Ni and PGE contents than most mantle-derived magmas.

The sulfide droplets collected at the base of intrusions and lava flows because they are denser than the silicate magma. The largest concentrations are typically found in locations where there are changes in the geometry of the contacts between intrusions or flows and the country rock. In some cases the accumulated sulfide liquid fractionated to form an Fe-rich monosulfide solid-solution (mss) cumulate and a Cu-rich sulfide liquid which later crystallized as an intermediate solid solution (iss). As a result of crystal fractionation of mss many Ni sulfide orebodies show a strong zonation with respect to Cu and PGE. During mss fractionation Os, Ir, Ru, and Rh concentrated in the mss cumulate and Cu, Pt, Pd, and Au concentrated in the Cu-rich sulfide liquid. The partition coefficient for Ni into mss is close to 1; thus, mss fractionation would not have caused large variations in Ni concentrations. The silicate magma solidified at or above 1,000°C whereas the Cu-rich sulfide liquid solidified at ~900°C. Thus, at many localities the Cu-rich sulfide liquid appears to have migrated into dilatent spaces in the footwall or the hanging wall to form veins that extend into the country rock for up to 2 km.

At subsolidus temperatures a number of processes modify the orebodies. Both the mss and iss are not stable below 600°C. As the sulfides cooled mss exsolved to form pyrrhotite and pentlandite (±pyrite), and iss exsolved to form chalcopyrite and pyrrhotite (±cubanite, ±pyrite). Most of the PGE and chalcophile elements that originally partitioned into mss or iss are not readily accommodated in the structure of pyrrhotite, pentlandite, and chalcopyrite; therefore, they exsolve from the mss and iss at low temperature and form a wide variety of platinum group minerals (PGM).

During deformation stress may focus in the structurally incompetent massive sulfide units, which are generally located at the lower contact of the mafic or ultramafic host rock. In this situation the massive sulfides may then be displaced relative to the host rocks. Finally, during greenschist to amphibolite metamorphism, olivine is unstable and Ni released from the olivine will partition into disseminated sulfides, thereby upgrading the sulfides.

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Introduction

Approximately 60 percent of the world's nickel is produced from Fe-Ni-Cu sulfides found in association with mafic or ultramafic intrusions or flows (Naldrett, 2004). This includes the Fe-Ni-Cu sulfides found at the margins of the Sudbury Igneous Complex, Ontario, Canada. Most of the rest of Ni production comes from limonitic and saprolitic laterite deposits, which form by weathering of ultramafic rocks (Freyssinet et al., 2005). A small quantity of Ni is produced as a by-product of platinum group element (PGE) deposits associated with layered intrusions (Cawthorn et al., 2005). Thus, mafic and ultramafic rocks ultimately represent the source of almost all the world's nickel resources. This paper focuses on the formation of Ni-Cu sulfide deposits.

There are many Ni-Cu sulfide deposits (i.e., accumulations of Ni-Cu sulfide minerals; Bates and Jackson, 1987) around the world, but most of these do not constitute Ni-Cu sulfide ore deposits (i.e., they are not economic at present to mine and process; Bates and Jackson, 1987) because they are either too small or the grade is too low, or other factors prevent the economic exploitation of the deposit. In this paper Ni-Cu sulfide ore deposits will be referred to as Ni sulfide ores, noneconomic Ni-Cu sulfide deposits as Ni sulfide occurrences, and when both ores and occurrences are included the term Ni sulfide deposits will be used. Most Ni sulfide ore deposits occur as a cluster of deposits known as a mining camp. Typically the grade of the ores is greater than 0.5 percent Ni and the mining camp generally contains more than 100,000 tons (t) Ni (Table 1). Each individual ore deposit generally contains greater than 10,000 t Ni.

Ni sulfide deposits have been studied extensively over the past 25 years, not only because of their significance with respect to Ni but also because many of these sulfides contain Au and PGE at the g/t level, Cu in the 0.1 to 10 percent range, and Co at the 0.1 to 0.3 percent level, making these elements valuable by-products of Ni production.

Naldrett (2004) summarizes much of the literature on magmatic sulfides, and Arndt et al. (2005) discuss the petrogenesis of mafic-ultramafic rocks and aspects relevant to their mineralization. Recent summaries of Ni-Cu sulfides associated with komatiites and picrites include Lesher and Keays (2002), Arndt et al. (2005), and Barnes (2004, in press). The Sudbury Igneous Complex has recently been the subject of a special issue of *Economic Geology* (Lesher and Thurston, 2002), and there are also numerous papers in a recent symposium volume edited by Lightfoot and Naldrett (1994). Details of the Noril'sk-Talanakh deposits are presented in various papers in the Lightfoot and Naldrett (1994) volume and summary papers by Czamanske et al. (1995) and Naldrett et al. (1996a); Jinchuan has been described by Chai and Naldrett (1992), Tang (1993), and De Waal et al. (2004). There are two recent special issues devoted to Voisey's Bay (Lambert and Ripley, 1999; Naldrett and Li, 2000). These papers provide detailed descriptions of individual deposits that are beyond the scope and aim of this paper. The objective of this paper is first to document the features that are common to most Ni sulfide deposits and then review the range and relative

Table 1. Estimates of Historic Production, Present Reserves, and Resources for Ni Sulfide Deposits and Camps

Mining Camp	Location	Size (mt)	Ni (wt %)	Cu (wt %)	Contained Ni (t)	% of total resources	Deposit type	References
Sudbury	Ontario, Canada	1648.0	1.2	1.03	19,776,000	30.34	1 (i)	1
Noril'sk-Talnakh	Russia	1309.3	1.77	3.57	23,174,610	35.55	1 (ii)	2
Jinchuan	China	515.0	1.06	0.67	5,459,000	8.37	1 (ii)	1
Voisey's Bay	Labrador, Canada	136.7	1.59	0.85	2,173,530	3.33	1 (iv)	2
Selebi-Pikwe	Botswana	110.0	0.75	1	825,000	1.27	1 (vi)	1
Shebandowan	Ontario, Canada	15.0	1.5	1	225,000	0.35	1 (vi)	1
Lynn Lake	Manitoba, Canada	20.0	1.02	0.535	204,000	0.31	1 (vi)	1
Monchegorsk	Russia	47.0	0.7	0.4	329,000	0.50	1 (vi)	1
Black Swan	Western Australia	10.9	3.43	0.15	373,870	0.57	2 (i)	4,3
Forrestania Belt	Western Australia	14.0	1.3	0.06	182,000	0.28	2 (i)	3
Honeymoon Well	Western Australia	128.0	0.79	0.008	1,011,200	1.55	2 (i)	4,3
Kambalda district	Western Australia	34.3	3.08	0.25	1,055,516	1.62	2 (i)	4,3
Lake Johnston	Western Australia	13.9	1.81	n.a.	251,228	0.39	2 (i)	4
Mt. Keith	Western Australia	503.0	0.55	0.01	2,766,500	4.24	2 (i)	4,3
Perseverance	Western Australia	129.1	0.97	0.06	1,252,270	1.92	2 (i)	4,3
Windarra	Western Australia	6.66	1.21	0.16	80,586	0.12	2 (i)	4,3
Widgiemooltha	Western Australia	21.1	1.66	0.17	350,094	0.54	2 (i)	4,3
Yakabindi	Western Australia	290.0	0.58	0.008	1,682,000	2.58	2 (i)	4,3
O'Toole	Brazil	6.6	2.2	0.4	145,200	0.22	2 (i)	5
Thompson Belt	Manitoba, Canada	89.0	2.5	0.13	2,225,000	3.41	2 (i)	1
Cape Smith (Raglan)	Quebec, Canada	18.5	3.13	0.88	579,050	0.89	2 (i)	1
Hunter's Road	Zimbabwe	30.0	0.7	na	210,000	0.32	2 (i)	1
Shangani	Zimbabwe	22.0	0.71	na	156,200	0.24	2 (i)	1
Trojan	Zimbabwe	20.4	0.68	na	138,380	0.21	2 (i)	1
Pechenga	Russia	36.0	1	0.4	360,000	0.55	2 (ii)	1
Kabanga	Tanzania	11.7	1.72	0.26	201,240	0.31	2 (ii)	1

Notes: n.a. = not available, 1 = Eckstrand (1996), 2 = Naldrett (2004), 3 = Marston et al. (1981, 4 = S.J. Barnes (in press), 5 = Brenner et al. (1990)

importance of the processes that are responsible for the generation of economically viable concentrations of Ni, Cu, and PGE in magmatic sulfides.

Classification of Ni Sulfide Deposits

Nickel-sulfide deposits may be divided into two broad classes on the basis of their composition and in particular on the basis of their Ni/Cu ratios. As explained later, this reflects the composition of the silicate magma from which the sulfide liquid segregated. All of the deposits of class 1 have Ni/Cu ratios in the 0.8 to 2.5 range (Table 1). Moreover, the concentration of Ni in rocks consisting of 100 percent sulfides ranges from 1 to 6 percent; thus, the S/Ni ratio in the rocks ranges from 6 to 36 (Table 2). With the notable exception of Jinchuan, Gansu Province, China, the host rocks for class 1 Ni sulfide deposits are gabbronorite or troctolite. Deposits of class 2 have Ni/Cu ratios greater than 3 (Table 1). In general the concentration of Ni in rocks consisting of 100 percent sulfides is in the 6 to 18 percent range, and thus the S/Ni ratio in the rocks is between 2 and 6 (Table 2). The host rocks for class 2 are ultramafic. Class 1 contains the bulk of the world's resources in just three mining camps; Sudbury, Noril'sk-Talnakh, Russia, and Jinchuan (Table 1, Fig. 1). Class 2 consists of many medium-sized to small deposits (Table 1).

We further divide Ni sulfide deposits based on their geologic association and rock type (Table 3). Subclass 1(i) contains only one mining camp, the Sudbury basin. It is the world's largest historic Ni producer and its production plus reserves make up approximately 34 percent of the world's resources (Table 1). The geologic setting of these Ni sulfide ores is at the margins of an igneous complex formed from an impact melt (Fig. 2a). Subclass 1(ii) consists of the Noril'sk-Talnakh and the Jinchuan Ni sulfide ores. This subgroup also contains a number of large tonnage but low-grade Ni sulfide occurrences such as those of the Duluth intrusion, Minnesota. These Ni sulfide deposits are typically found at the base of sills and margins of dikes that are largely gabbroic in composition. The sills and dikes are thought to be located in continental rifts and to represent the feeder conduits of higher level intrusions or continental flood basalts (Fig. 2b). In the case of Jinchuan, the host rock is a peridotite and it is argued that the sulfides were emplaced along with an olivine crystal mush (De Waal et al., 2004). The third subclass, 1(iii), is also found in feeders in a rift, but in this case a rifted back arc rather than a continent. There are no known Ni sulfide ores although there are numerous occurrences that have significant Ni grades, e.g., Bruvann deposit in the Råna intrusion, Norway (S-J. Barnes et al., 1988) and the many small Ni sulfide occurrences in the Baby-Belleterre belt, Quebec, Canada (Barnes et al., 1993). The fourth subclass 1(iv) contains the Voisey's Bay Ni sulfide ores of Labrador, Canada. These sulfides are associated with a troctolite dike and intrusion (Fig. 2c). The intrusion was emplaced into the suture zone between the Nain and Churchill provinces some 500 m.y. after the collision of the two provinces (Ryan et al., 1995). Subclass 1(v) contains no known Ni sulfide ores. It consists of small intrusions that appear to have been emplaced into thick crust (Fig. 2d). There are many examples of these in the Sveconorwegian terrane of Scandinavia (e.g., Flåt, Erterlien; S-J. Barnes et al., 1988) and the Grenville

FIG. 1. Location of some of the world's Ni mining camps and ore deposits.

TABLE 2. Estimated Compositions of Sulfides Fraction from Some Ni Deposits

	n	S (%)	Fe (%)	Ni (%)	Cu (%)	Ag (ppm)	As	Co	Sb	Se	Zn	Os (ppb)	Ir	Ru	Rh	Pt	Pd	Au	Ref
Sudbury, Strathcona deposit, Class 1 (i)																			
Dissseminated	2	38.16	52.64	4.08	5.13	n.a.	80	2522	369	74	3791	101	211	469	452	3684	4324	1651	1
Massive	37	n.l.	n.l.	3.63	1.23	n.a.	n.a.	1500	n.a.	n.a.	233	8	14	21	30	858	882	100	2
Fe-rich	10	n.l.	n.l.	3.10	0.37	n.a.	n.a.	2100	n.a.	n.a.	n.a.	20	29	52	60	114	105	19	2
Cu-rich	32	n.l.	n.l.	1.97	28.27	n.a.	n.a.	300	n.a.	n.a.	2750	<0.5	0.11	<2	<0.16	4710	5213	296	2
Noril'sk-Talnakh, Oktabr'sky deposit, Class 1 (ii)																			
Disseminated	11	37.14	46.14	3.35	13.37	61	0.86	1558	0.52	n.a.	477	57	46	136	321	6808	25184	4307	3
Massive and matrix	33	37.24	55.71	3.63	12.27	47	2.30	1400	0.52	111	322	30	24	63	259	9421	29049	1217	3
Fe-rich Pd/Ir < diss	23	37.97	57.98	4.07	6.24	13	0.51	1657	0.15	70	187	30	31	81	339	2602	12435	238	3
Cu-rich Pd/Ir > diss	10	35.55	42.43	2.63	26.15	126	6.43	809	1.37	123	631	28	9	21	75	25103	67260	3470	3
Vein	2	34.73	35.85	2.65	32.21	75	5.07	690	0.89	n.a.	384	<1	1.10	6	22	28395	38821	2249	3
Voisey's Bay, Eastern Deeps deposit, Class 1 (iii)																			
Disseminated	25	n.l.	n.l.	6.08	3.32	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	10	6	31	19	360	354	355	4
Massive	12	n.l.	n.l.	3.32	1.15	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	15	7	26	18	34	144	18	4
Basal breccia sulfide	44	n.l.	n.l.	4.4	2.47	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	9	5	37	13	242	264	245	4
Western Australia, Perseverance deposit, Class 2 (i)																			
Disseminated	12	37.54	51.56	10.15	0.53	n.a.	n.a.	2410	n.a.	n.a.	n.a.	131	100	227	52	671	1412	56	5
Massive and matrix	15	38.19	53.66	7.72	0.20	n.a.	n.a.	1849	n.a.	n.a.	n.a.	199	158	420	113	176	374	27	5
Breccia	9	38.07	52.65	8.90	0.18	n.a.	n.a.	1958	n.a.	n.a.	n.a.	184	143	420	98	205	575	31	5
Cape Smith, all deposits, Class 2 (i)																			
Disseminated	89	36.99	48.21	11.43	3.38	14	142	3000	34.54	116	1436	351	264	1553	625	3530	9581	380	3
Massive and matrix	57	37.74	51.90	8.40	1.95	3	6		2.06	122	181	146	117	717	483	2052	3227	72	3
Fe-rich Pd/Ir < diss	32	37.77	52.15	8.65	1.43	2	7		1.53	113	171	173	154	917	601	1542	1907	54	3
Cu-rich Pd/Ir > diss	17	37.67	51.23	7.82	3.28	3	4		2.32	135	176	86	49	271	238	3375	6079	125	3
Vein	5	35.17	38.73	17.16	8.95	36	53		17.37	76		26	11	75	71	1985	14961	3734	3
Pechenga, all deposits, Class 2 (ii)																			
Disseminated	21	37.08	47.72	8.15	3.57	30	37	2477	3.97	75	481	26	26	57	36	917	998	156	6
Massive	16	37.24	49.19	9.43	2.07	18	29	2132	0.65	82	219	63	47	103	57	333	417	69	6
Sulfide separates	15	37.43	50.17	8.69	1.95	8	22	2008	0.50	82	144	62	41	118	51	375	346	101	6
Fe-rich Pd/Ir < diss	12	37.34	49.50	8.78	2.18	15	26	2112	0.74	72	265	99	63	135	65	208	258	43	6
Pd/Ir > diss	4	36.94	48.28	11.72	1.77	34	42	2193	0.43	120	124	17	21	49	38	1383	1766	288	6
Breccia matrix	18	37.75	51.67	7.40	1.31	17	68	1778	1.00	73	290	39	35	61	48	467	443	109	6
Vein	1	34.43	28.58	2.96	34.02	90	7	405	0.24	67	1392	442	221	511	122	223	51	42	6
Sedimentary	6	52.51	44.20	0.22	0.31	3	121	219	10.74	21	1309	<6	2	<10	<10	30	30	50	6

Notes: n.l. = the metal values were reported reculated to 100% sulfides but Fe and S were not reported, n.a. = no analyses; Ref: 1= this work, 2 = Li et al. (1993), 3 = Barnes (1997b), 4 = Naldrett et al. (2000), 5 = S.J. Barnes et al. (1988), 6 = Barnes et al. (2001b)

TABLE 3. Classification of Ni Deposits

Class	Host body	Geologic association	Ni/Cu	S/Ni	Examples of producers	Examples of occurrences
1(i)	Gabbronorite	Astrobleme	~1	>6	Sudbury	
1(ii)	Gabbronorite, minor peridotites and pyroxenites	Rift, feeders to contintental flood basalts	0.5-2	>6	Noril'sk Jinchuan	Duluth Muskox Insizwa
1(iii)	Gabbronorite, minor peridotites and pyroxenites	Rifted back-arc basin, feeders	1-2	>6	Bruvann	Baby-Belleterre
1 (iv)	Gabbronorite to anorthosites	Province boundary feeder	1-2	>6	Voisey's Bay	
1 (v)	Gabbronorite to anorthosites	Thick crust	1-2	>6	None known	Flat Lac Volant
1 (vi)	Gabbronorite, minor peridotites and pyroxenites	Deformed or unkown	1-2	>6	Selebi-Pikwe Vammala	Kotalahti
2 (i)	Peridotite-pyroxenite, minor dunite	Rift, komatiite flows, and intrusions	10-20	<6	Kambalda, Thompson Cape Smith	Alexo, Texmont
2 (ii)	Pyroxenite-peridotite, minor gabbro	Rift, picrite flows, and intrusions	3-10	<6	Pechenga Kabanga	

terrane of Canada (e.g., Lac Kenogami,Vaillancourt, 2001; Lac Volant, Nabil et al., 2004). Some have a reasonable Ni grade but none have large tonnage. The final class 1(vi) consists of Ni sulfide deposits associated with gabbronorites that are highly deformed or for which too little information has been published to provide a classification that relates to geologic setting. The two Ni sulfide ores in this class are Selebi-Pikwe, Botswana, and Vammala, Finland. Historically, many small deposits of this type were mined in Scandinavia and Finland (Papunen, 1989).

Class 2 deposits, associated with ultramafic rocks, may be subdivided into those deposits associated with komatiites [2(i)] and those associated with picrites [2(ii)]. There are two differences between the picritic and komatiite hosts. First, by definition, picrites contain a large quantity of olivine phenocrysts while komatiites do not necessarily contain olivine phenocrysts. Second, picritic magmas are enrichment in incompatible elements, such as alkalis and light rare earth elements (LREE). Importantly, the picrites that host Ni sulfide ores are not alkalic. Most komatiitic Ni sulfide ores are thought to be formed at the base of flows. In this group we find the Norsemen-Wiluma and Southern Cross-Forrestania greenstone belts of Western Australia, the Thompson nickel belt deposits of Manitoba, and the Cape Smith deposits of northern Quebec (Fig. 1). The host bodies to some of the deposits containing <1 percent Ni from Western Australia (e.g., Mt. Keith) may be intrusions (Rosengren et al., 2005). In the picritic class are included the Pechenga deposits of the Kola peninsula, Russia, and the Kabanga deposit of Tanzania. The geologic setting for these types of deposits is probably a rift zone that has a coincident plume (Barnes et al., 1997b, 2001b).

It is notable that all the known Ni sulfide ore deposits, except Sudbury, are associated with rocks of the tholeiitic or komatiitic/piciritc lineages. There are no known ore deposits associated with mid-ocean ridge basalts (MORB), ophiolites, and calc-alkaline or alkaline rocks. There are Ni occurrences that have been mined in the past, such as at Acoje in the Zambales ophiolite, Philippines (Yumul, 2001). Furthermore, Peltonen (2004) states that many of the Ni sulfide occurrences in Svecofennian terrane of Finland formed above a subduction zone and were derived from calc-alkaline magmas, although none are currently economic. Typically, the geologic setting of Ni sulfide ore is a region where a large volume of mafic magma has had access to continental crust, such as a rift or along a crust-penetrating fault zone.

General Characteristics of Magmatic Ni-Cu Sulfide Deposits

The minerals that host Ni and Cu in magmatic deposits are base metal sulfides. In most cases the mineral assemblage consists of an intergrowth of pyrrhotite (Fe_7S_8), pentlandite ($[FeNi]_9S_8$), and chalcopyrite ($FeCuS_2$; Fig. 3a). In a few cases such as at Noril'sk-Talnalk, the Cu-bearing minerals are more varied, including cubanite (Fe_2CuS_3), mooihookite ($Cu_9Fe_9S_{16}$), and talnakhite ($Cu_9[Fe,Ni_8]S_{16}$). Associated with these sulfides in most cases is 1 to 15 percent magnetite (Fig. 3b). Cobalt, PGE, and Au are extracted from most magmatic Ni-Cu ores as by-products, with significant impact on economics in some deposits (e.g., the Noril'sk-Talnakh deposits produce much of the world's Pd). The Co is found in pentlandite and substitutes for Ni up to the percent level. The PGE are generally present as platinum group minerals (PGM), in the form of small grains of PGE-containing sulfides, arsenides, antimonides bismithides, and tellurides, which exsolved from the base metal sulfides and occur at or near grain boundaries (Cabri, 2002; Makovicky, 2002). In many cases a large proportion of

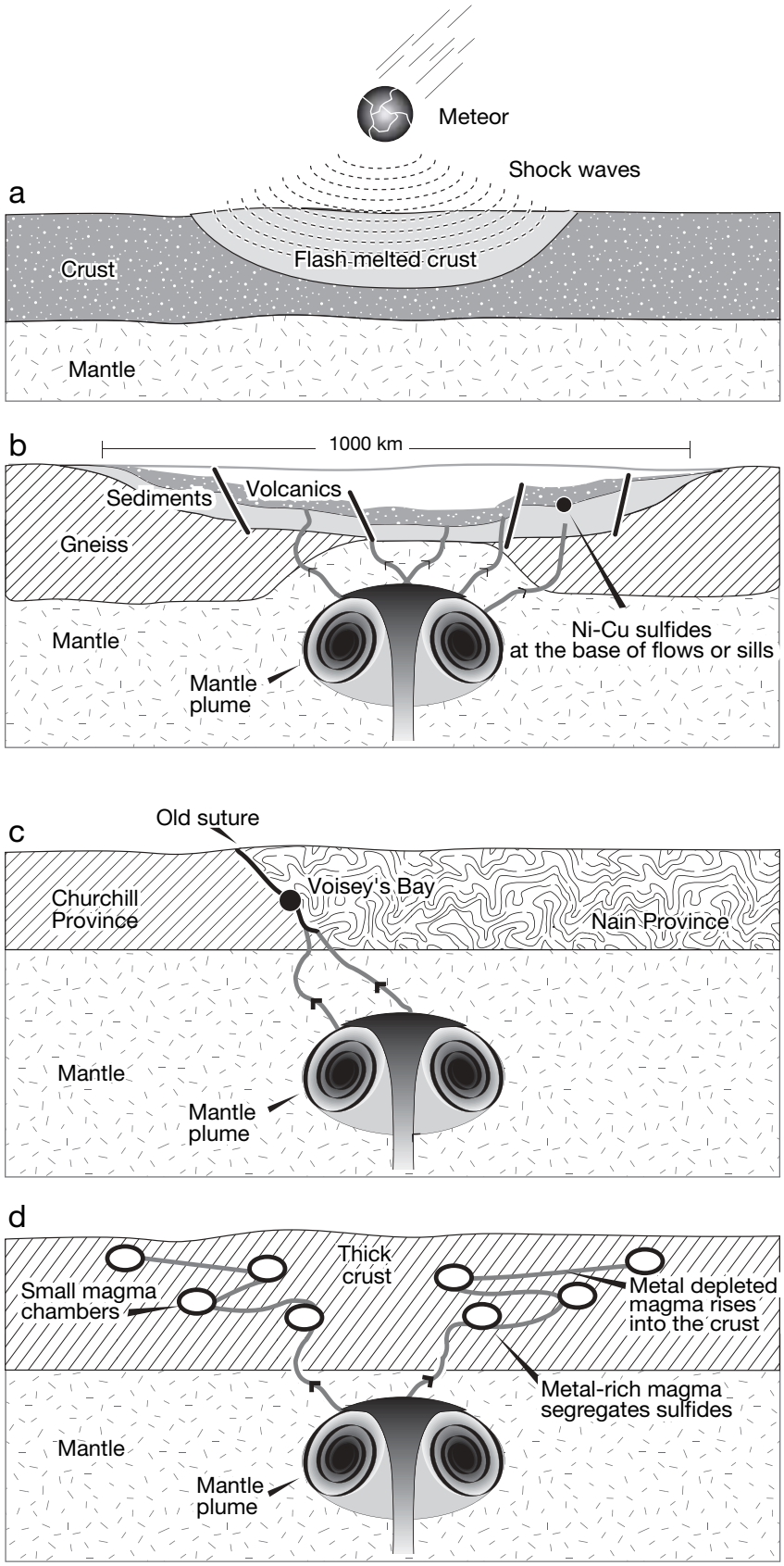


FIG. 2. Cartoons of the geologic settings of Ni sulfide deposits. a. Meteor impact, Sudbury. b. Feeders to flood basalt, e.g., Noril'sk. c. Feeders along a suture, Voisey's Bay. d. Thick crust, Grenville.

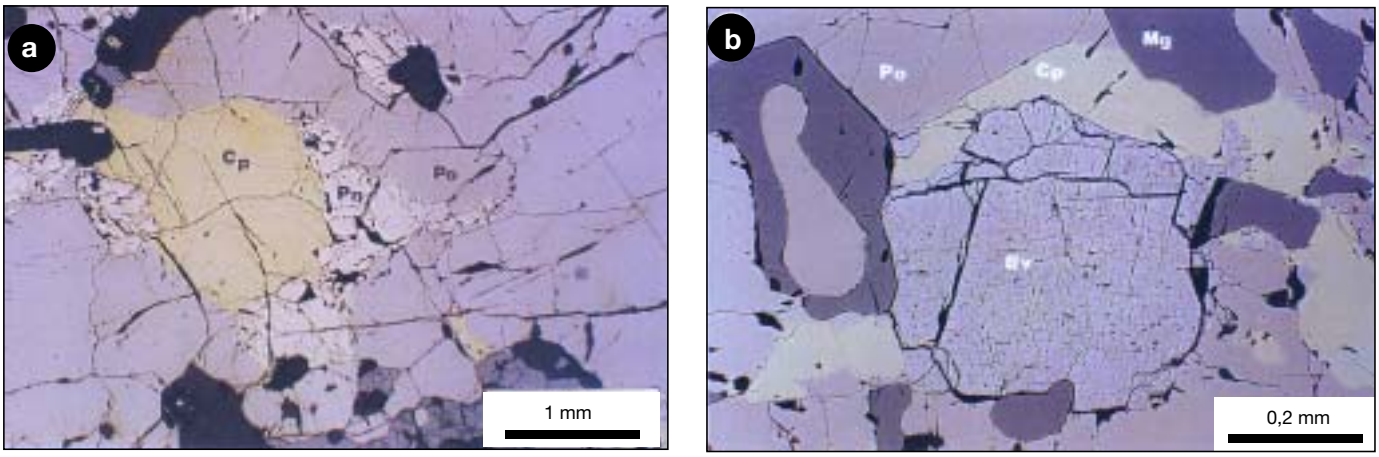


FIG. 3. Photomicrographs of base metal sulfides and associated oxides from Ni sulfide deposits: pyrrhotite (Po), pentlandite (Pn), chalcopyrite (Cp), bravoite (Bv), and magnetite (Mg). a. Massive sulfides from Voisey's Bay. b. Massive sulfides from Lac Volant.

the Pd is contained in solid solution in pentlandite (Paktunc et al., 1990; Distler, 1994).

The primary sulfide mineralogy may be modified by alteration and/or metamorphism. In deeply weathered terranes the supergene sulfide minerals may have lost S or base metals. The mineralogy may consist of bravoite (Fig. 3b), violarite, and in some case native Cu or Cu oxides. In metamorphosed environments, the Fe-sulfides may be oxidized and magnetite replaces pyrrhotite (e.g., Cawthorn and Meyer, 1993; Maier and Barnes, 1996).

Sulfides tend to be concentrated in the lower portions of the intrusions or flows in which they occur and in many cases are associated with physical depressions or changes in geometry of the topography of the footwall (e.g., the Talnakh deposits; Fig. 4b). The highest concentrations of sulfides tend to occur either at the base of the host body or in the immediate footwall. At most Ni sulfide deposits the sulfide may be divided into disseminated, matrix or net, and massive sulfide, based on a combination of the sulfide content of the rock and the silicate texture (Fig. 5). When the sulfides are not interconnected they are described as disseminated. The amount of sulfide present is between 1 and 33 modal percent (Fig. 6a). When sulfides are interconnected and form a matrix to the silicates they are described as matrix or net textured (Fig. 6b). The sulfide is generally 33 to 66 percent, although it can be lower in some cases. When the sulfide content exceeds 66 percent they are described as semimassive to massive sulfides (Fig. 6c). Due to the density difference between silicate and sulfide minerals there is a difference between modal percent and weight percent of a phase. Assuming that the average S content of the sulfides is 38 percent, these modal divisions correspond to approximately 0.6 to 17 wt percent S in rocks containing disseminated sulfide, 17 to 28 wt percent S in rocks containing matrix (or net) sulfide, and 28 to 38 wt percent S in rocks containing massive sulfide.

Disseminated sulfides may be further divided. In most cases they occur as irregular 1-mm to 1-cm patches interstitial to the silicate and oxide minerals. At some localities, notably Noril'sk-Talnakh, Pechenga, and Insizwa, South Africa, they occur as 1- to 10-cm-sized globules. In a few cases these globules are zoned with a pyrrhotite-rich base and chalcopyrite-rich top (Fig. 6a). This zonation is mirrored on a much larger scale in the massive ores, which may form a pyrrhotite-rich base or margin and chalcopyrite-rich top or center (e.g., the Oktyabr'sky ore deposit at Noril'sk-Talnakh). The massive ores tend to occur along the contact between the country rock and the host rocks. However, massive sulfide may also occur in footwall veins (Figs. 5, 6d) that in some cases extend away from the contact into the country rock for up to 2 km (e.g., Sudbury).

In cases where the magma has been emplaced into or onto a sulfide-bearing sedimentary rock (e.g., Duluth, Pechenga, Thompson, and Kambalda, Western Australia) there is a fifth category of sulfides (Fig. 6e). Away from the intrusions in their unmetamorphosed form the sulfide is pyrite (e.g., Duluth and Pechenga; Theriault and Barnes, 1998; Barnes et al., 2001b; Ripley and Li, 2003). However, close to the intrusion contact the pyrite is converted to pyrrhotite and locally grades into Ni-rich sulfides, e.g., Thompson (Bleeker, 1990).

Deformation can also complicate the relationship between the sulfide and silicate minerals. Massive sulfides sandwiched between country rock and a mafic or ultramafic host rock represent an incompetent layer that will tend to focus deformation and in many cases become a matrix to the brecciated silicate rocks (Fig. 6f). This texture has also been referred to as "durchbewegung" (Vokes, 1969) and is an especially common feature in the Thompson and Pechenga deposits.

Description of Representative Mining Camps

In most cases mining camps consist of a number of Ni sulfide ore deposits. Five of these camps will now be described in more detail.

Noril'sk-Talnakh

The Noril'sk-Talnakh Ni sulfide ores of Russia are found at the base of differentiated sills, which are dated at 248 ± 4 Ma (Campbell et al., 1992) and are associated with the Siberian continental flood basalts. Three of these intrusions (Noril'sk I,

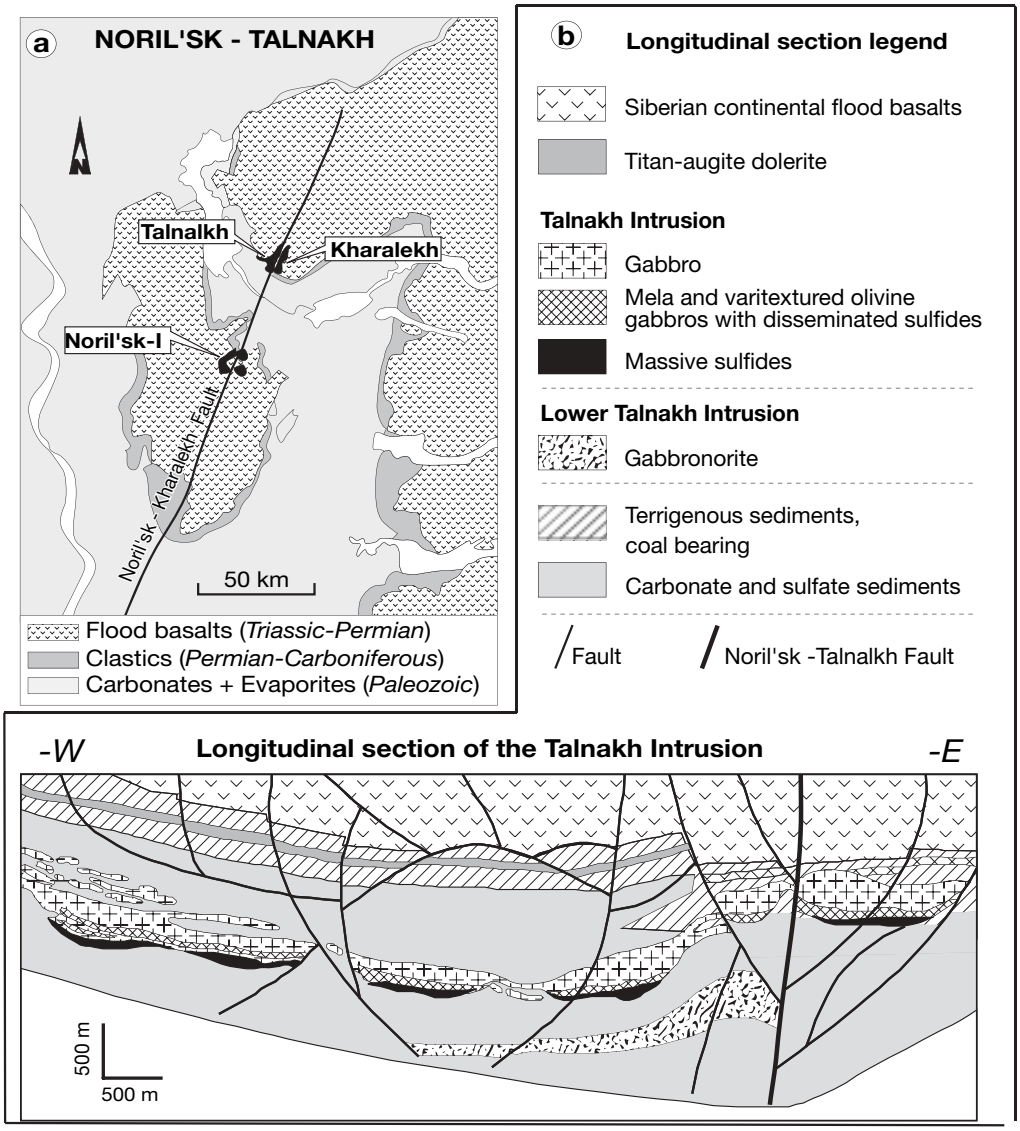


FIG. 4. a. Map of the Noril'sk-Talnakh district, showing location of the ore-bearing intrusions, modified after Zientek et al. (1994). b. Cross section of the Talnalk deposit, showing that sulfides are concentrated in embayments (modified after Duzhikova, 1992).

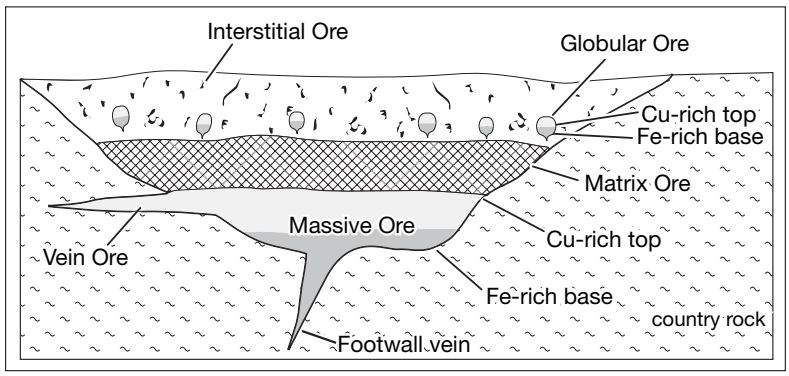


FIG. 5. Idealized sketch of the relationship between massive, matrix, disseminated, and vein sulfides (modified after Barnes et al., 1997b).

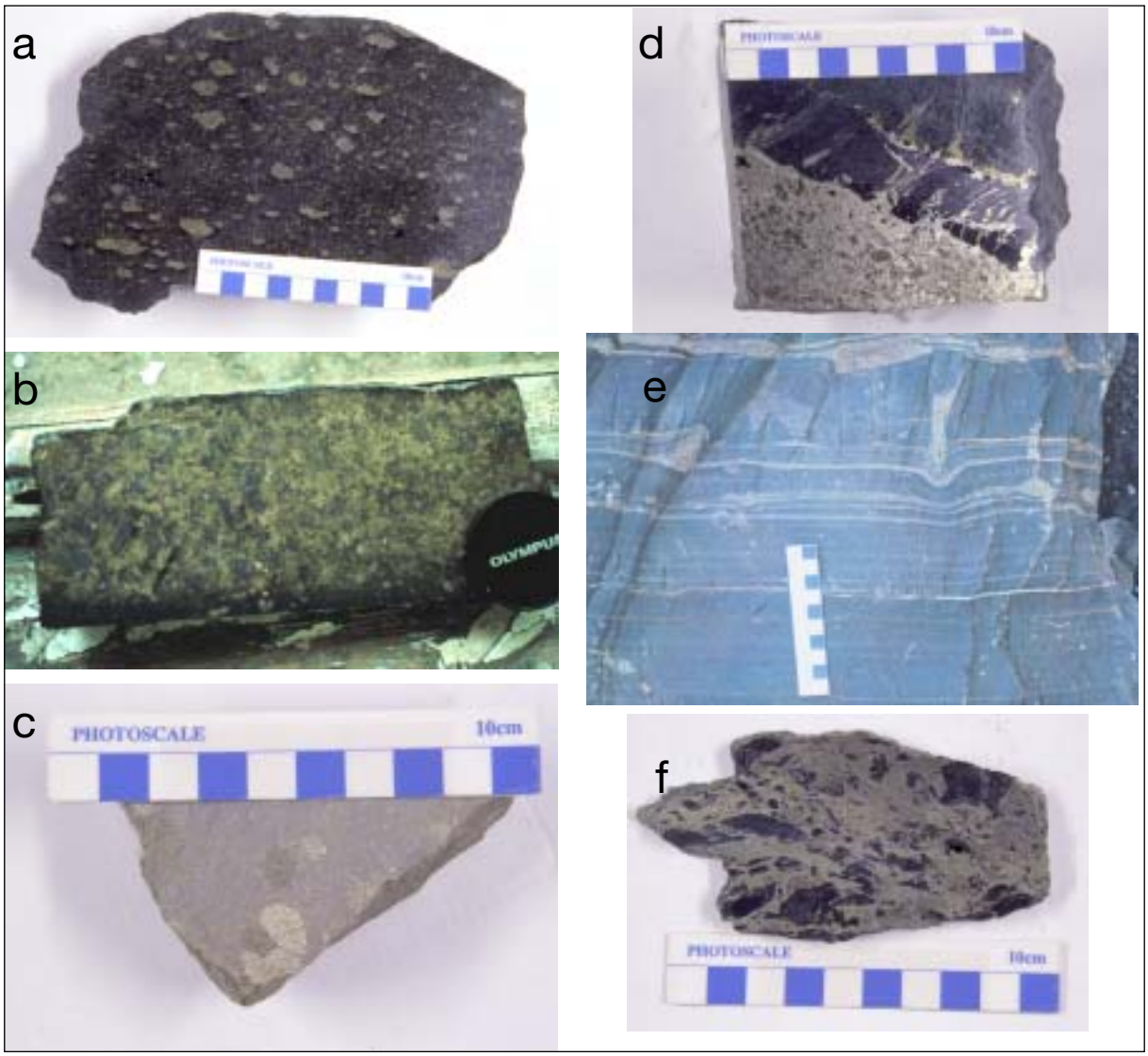


FIG. 6. Photographs. (a) disseminated, (b) matrix, (c) massive, (d) vein, (e) sedimentary, and (f) breccia matrix sulfides. The matrix sulfides are from Noril'sk, all of the others examples are from Pechenga.

Talnakh, and Kharaelakh; Fig, 4a) contain ore deposits (Zientek et al., 1994). Many other intrusions in the area also contain disseminated sulfides, but only these three contain sufficient sulfides of high enough grade to be mineable. The three ore-bearing intrusions occur along a major crust-penetrating fault, which is approximately 100 km long and known as the Noril'sk-Talnakh fault (Fig. 4a). The country rocks include evaporites, carbonates, and coal-bearing terrigenous sediments that range in age from Devonian to Carboniferous. The geology of the whole area has been interpreted as having formed in a depression associated with a rift structure related to traces of deep faults (Duzhikov et al., 1992).

The ore-bearing intrusions are 50 to 300 m thick, 500 to 2,000 m wide, and over 15 km long (Fig. 4b). A typical cross section (Fig. 7) of the Talnakh intrusion has 3 to 10 m of massive sulfide at the base. This is overlain by a variable-textured olivine gabbro that contains disseminated sulfides. This variable-textured rock is characterized by irregular changes in texture, mode, and grain size on the scale of hand specimen to outcrop, and in many cases the unit contains inclusions of mafic rocks. The local term for this texture is taxitic (Zientek et al., 1994). The variable-textured olivine gabbro is overlain by an olivine melagabbro with disseminated sulfides. The Russian geologists refer to this as picritic gabbrodolerite (Zientek et al., 1994). Inclusions of the variable-textured olivine gabbro occur within the olivine melagabbro, suggesting that the olivine melagabbro magma was injected into the partly solidified variable-textured olivine gabbro. Above the olivine melagabbro the olivine concentration in the gabbro decreases and the unit consists of biotite-bearing olivine gabbro to gabbro. The rocks close to the upper contacts of the intrusions have variable crystal size and contain local domains of pegmatite and leucogabbro. These rocks are also referred to as taxitic by Russian geologists, because of their variable textures.

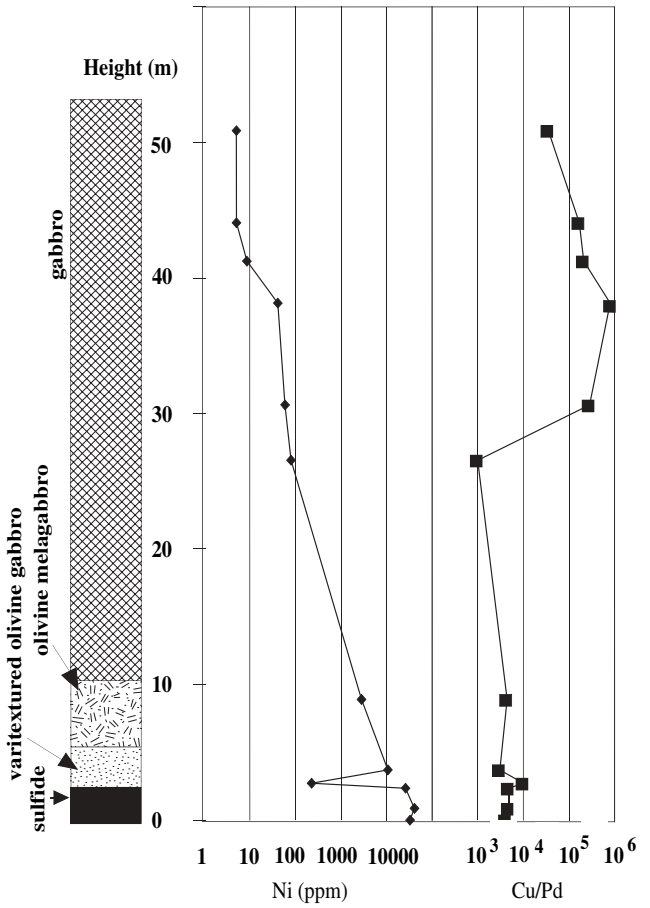


FIG. 7. Cross section of Talnakh intrusion from borehole 1799, showing changes in principle rock types, Cu/Pd ratio, and Ni content with height. Note how the Cu/Pd ratio in the gabbro overlying the ore deposit is lower than the mantle ratio, indicating that the magma has segregated sulfides and that a sulfide deposit may be present at depth.

The proportion of sulfide to silicate minerals present in the sills (~1:10) is far too high for the sulfides to have segregated from only the material in the sills (Likhachev, 1973; Naldrett et al., 1996a). Two models may be advanced to explain the disproportionate quantity of sulfides present. In the first model it is assumed that the sills are open systems and that a large quantity of silicate magma carrying olivine and plagioclase phenocrysts plus sulfide droplets passed through the sills. The sulfides droplets settled out of the silicate magma and collected in the topographic lows of the footwall (Zen'ko and Czamanske, 1994). However, in many cases the massive sulfides do not show concordant contacts with the intrusion and do not grade into matrix and disseminated sulfides of the sill. Furthermore, at some localities the massive sulfide crosscuts the contact between the sedimentary rocks and the intrusion. At other localities a thin slice of hornfels or fine-grained gabbro is present between the intrusion and the massive sulfides. This has led to an alternative model, which suggests that the sulfide liquid segregated from the silicate magma elsewhere and that this sulfide liquid was later injected between the consolidated sills and the sedimentary rocks. However, Zen'ko and Czamanske (1994) point out the disseminated sulfides from within a particular intrusion and the massive sulfides associated with it have the same isotopic (Re-Os, Pb-Pb) signatures, and different intrusions have slightly different signatures. This suggests to us that the massive sulfides segregated from the magma that formed the associated intrusion. The field relationships may be explained as follows. A Cu-rich sulfide liquid does not solidify until ~900°C, whereas the silicate magma might be expected to solidify by ~1,000°C. Thus, sulfide droplets could have segregated from the silicate magma as it flowed over embayments, such that the droplets formed a pool of liquid. The silicate magma could have solidified, followed by minor movements in the crust associated with the emplacement of the huge volume of flood basalts, causing the unconsolidated sulfide liquid to migrate short distances into any dilatencies that formed.

Voisey's Bay

The Voisey's Bay Ni sulfide ore deposits in Labrador are associated with a troctolite intrusion emplaced in the suture between the Protorozoic Churchill and Archean Nain provinces (Fig. 8a). The troctolite is much younger (1332.7 ± 1 Ma; Amelin et al., 1999) than the suture (1860–1840 Ma; Ryan et al., 1995) and is part of the Nain Plutonic Suite. The suite consists of troctolite, anorthosite, diorite, and granite, and it invaded the suture between 1350 and 1290 Ma (Ryan et al., 1995). The western end of the Voisey's Bay troctolite is emplaced in a Protorozoic paragneiss (the Tasiuyak gneiss) and the eastern end into orthogenesis and granite (Fig. 8b).

There are two general environments where sulfides have accumulated in the Voisey's Bay troctolite. One is within the 5- to 120-m-wide dike in the western part of the intrusion, where four mineralized zones have been found, the Reid Brook, Discovery Hill, Mini-Ovoid, and Ovoid orebodies (Fig. 8b). The other is at the margins of the Eastern Deeps intrusion, where the feeder dike enters the intrusion. Figure 8c shows a cross section of the Eastern Deeps intrusion. The feeder conduit contains a variable-textured troctolite in which the crystal size ranges from pegmatitic (up to 50 mm) to medium,. Patches of sulfides are present in much of the variable-textured troctolite. Massive sulfide and matrix sulfide occurs where the dike enters the chamber. The massive sulfide is surrounded by a breccia consisting of fragments of gneiss, unmineralized troctolite, and peridotite in a matrix of sulfide-bearing troctolite (Naldrett et al., 1996b). The bulk of the Eastern Deeps intrusion is occupied by a uniformed textured troctolite, referred to as normal troctolite.

Cape Smith

The Cape Smith fold and thrust belt of northern Quebec (Fig. 9a) was formed in the Paleoproterozoic (1900–1960 Ma; Parish, 1989). The southern portion of the belt consists of sedimentary rocks of the Lamarche Group, overlain by the continental flood basalts, alkali basalts, and shelf sedimentary rocks of the Povungnituk Group (Francis et al., 1983; Picard et al., 1990). The Povungnituk Group is in turn overlain by the Chukotat Group which consists of komatiitic basalts at the base and mid-ocean ridge basalts (MORB) toward the top (Francis et al., 1983; Picard et al., 1990). Nickel-sulfide deposits are found in two different settings in the belt known as

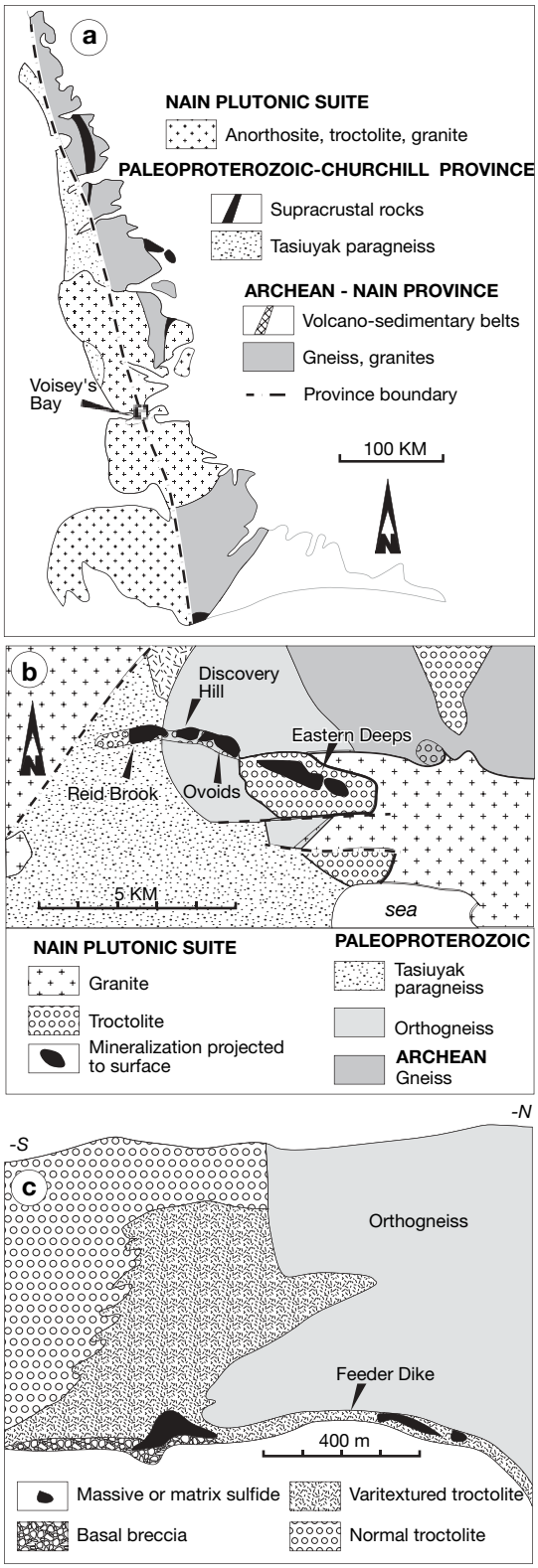


FIG. 8. a. General geology of the Voisey's Bay deposits; note that deposits are located on the suture between the Nain and Churchill provinces (modified after Ryan et al., 1995). b. Local geology of the Voisey's Bay deposits, showing projection to surface of the mineralization. c. Cross section through the Eastern Deeps deposit (modified after Lightfoot and Naldrett, 1999; later granite intrusion removed for simplicity). Note that the sulfides are concentrated where the feeder dike enters the chamber.

the Raglan and Delta horizons (Giovenazzo et al., 1989). The Raglan horizon consists of the Cross Lake, 2–3, Katinniq, and Donaldson Ni sulfide deposits and occur at the base of komatiitic basalt lava flows (Lesher et al., 1999). The Delta horizon consists of the Delta, Bravo, Mequillon and Expo Ni sulfide occurrences. The Delta horizon is found within the Povungnituk Group, at the base of sills and dikes of komatiitic basalt composition. These sills and dikes are interpreted as feeders to the overlying Chukotat Grop komatiite basalts (Francis et al., 1983; Giovenazzo et al., 1989, Barnes et al., 1992). In both settings the deposits are associated with siltstones and shales of the Povungituk Group., which consist predominantly of siltstone and shale.

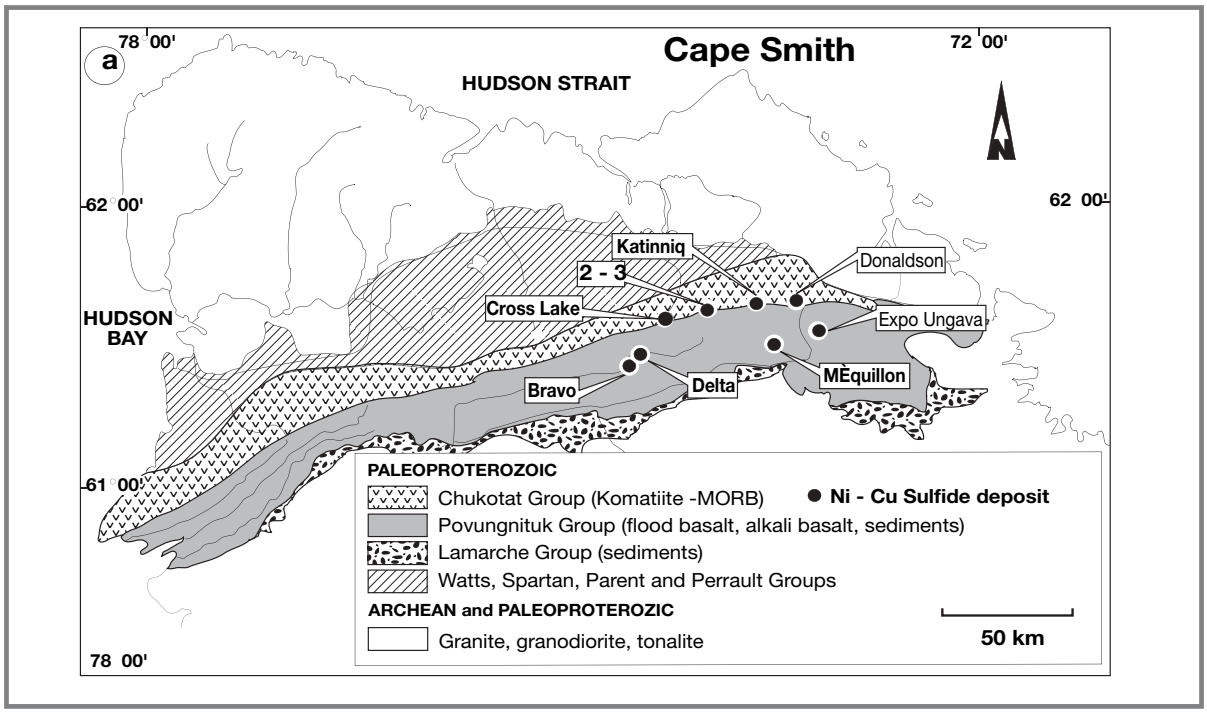
Figure 9b shows a cross section of the Katinniq deposit. Massive and matrix sulfides occur at the base of olivine mesocumulates generally in embayments at the base of a flow. The sulfide-rich zones are 10 to 50 m thick, approximately circular, and up to 200 m in diameter. The olivine mesocumulates are 100 to 200 m thick and are thought to represent the accumulation of olivine from komatiitic basalt flows. The lower chill zone consists of pyroxenite, whereas the upper chill margin consists of flow breccia in some places and microspinifex in other places. Lesher et al. (1999) interprets the mesocumulates at Katinniq as accumulations of olivine from a number of irruptions which followed lava channels through which large amounts of magma flowed. A very similar model has been used in many of the western Australian komatiite deposits (e.g. Lesher et al., 1984; S.J. Barnes, in press). Green and Dupras (1999) have taken this model even further and suggested that all the deposits of the Raglan horizon formed as part of a single 60-km-long lava channel.

Pechenga

The Pechenga greenstone belt is a part of the larger, discontinuously developed Paleoproterozoic Transfennoscandian greenstone belt, which stretches over a distance of 1000 km into the Kola peninsula of Russia. The northern part of the belt consists of clastic sedimentary rocks, alkali basalts, and flood basalts (Kolasjoki Formation; Fig. 10a). These are overlain by black shales, now pyrite-bearing graphitic schist, of the Pilguarvi Formation. Intruded into and erupted on to the black shales are ultramafic intrusions and flows. Nickel sulfide deposits are found at the base of some of the intrusions and flows (Fig. 10a). Overlying the black shales are basalts of MORB composition.

More than 226 differentiated ultramafic-mafic bodies have been counted within the graphitic pyrite-bearing sediments of the Pilgujärvi Formation. Twenty-five of these ultramafic bodies contain Ni sulfide ores and 68 contain Ni sulfide occurrences, whereas 113 are described as "barren" (Zak et al., 1982).

The ultramafic bodies have been dated at 1977 ± 52 Ma (Sm-Nd and Pb/Pb on mineral separates; Hanski, 1992). The ultramafic bodies at the west end of the belt are interpreted to be extrusive and those in east end as intrusive (Hanski and Smolkin, 1989; Melezhik, et al., 1994). The intrusions are referred to as gabbro-wehrlites (e.g., Smolkin, 1977), and the flows have been termed "ferropicrites" (Hanski and Smolkin, 1989). The ferropicrite flows are weakly differentiated, whereas the intrusions are well-differentiated gabbro-wehrlite



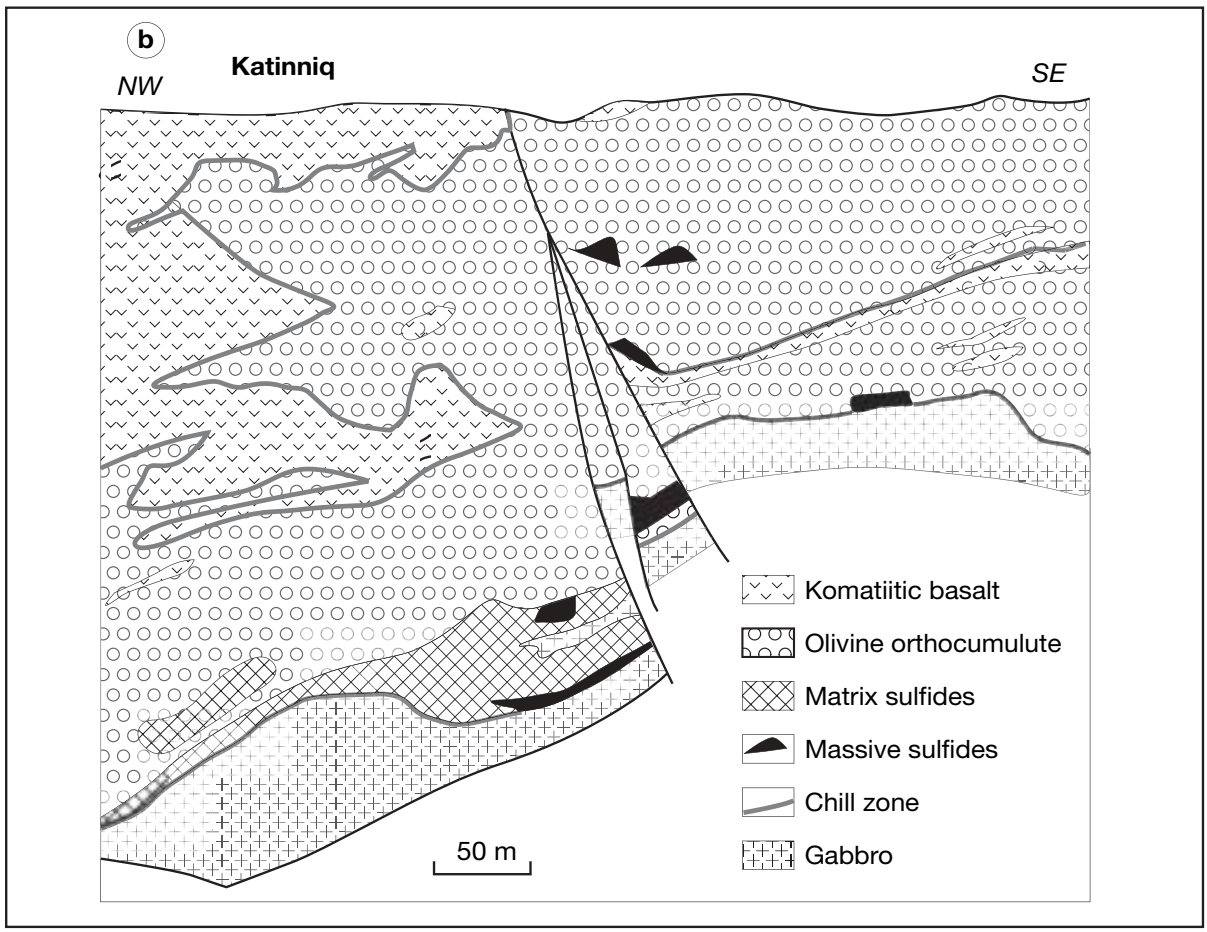


FIG. 9. a. Regional geology of the Cape Smith fold belt, showing the location of sulfide deposits and occurrences (modified after Lamothe, 1986). b. Cross section through the Katinniq deposit (modified after Gillies, 1993).

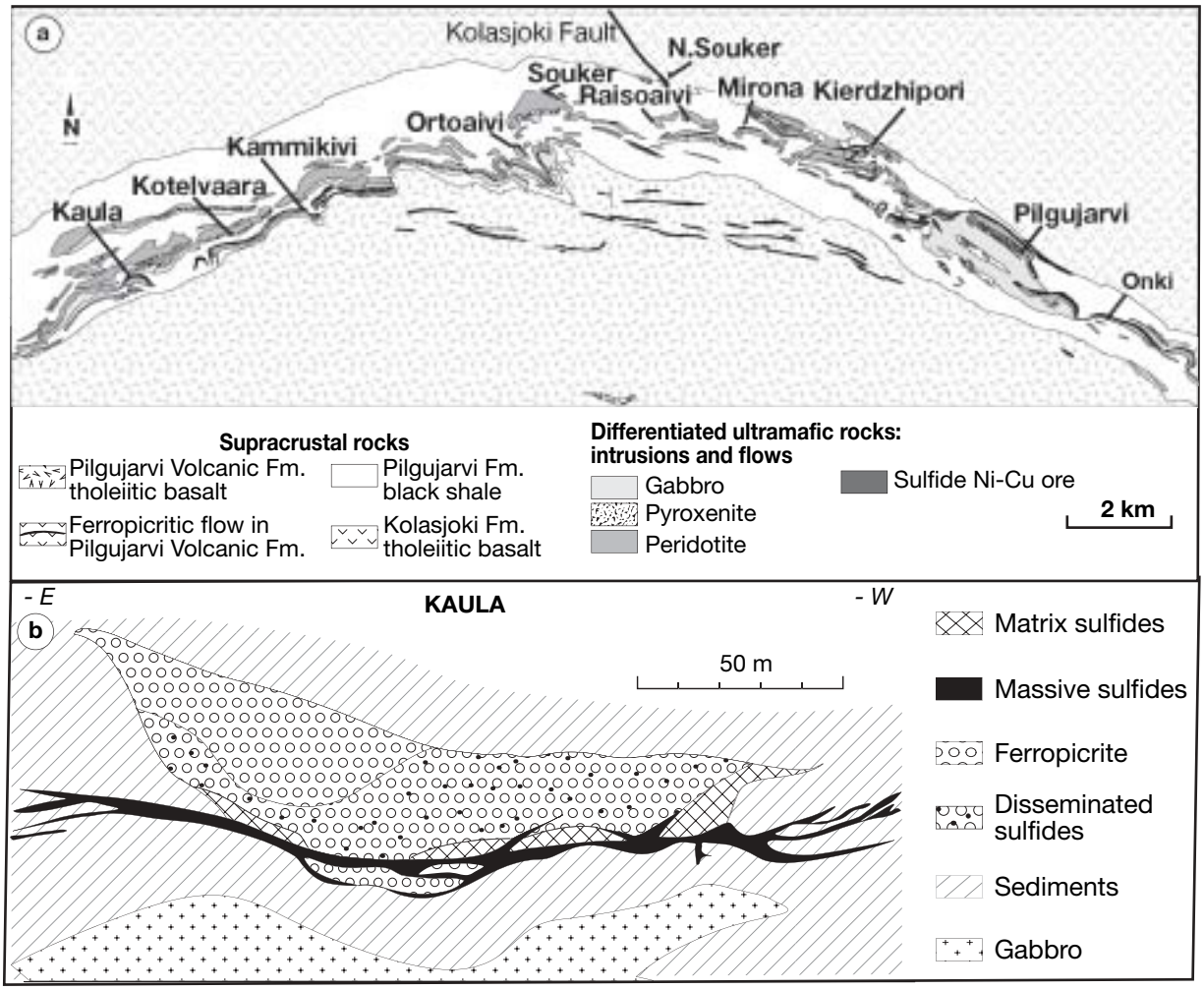


FIG. 10. a. Geology of the Pechenga mining camp (modified after Barnes et al., 2001b). b. Plan of the Kaula ore deposit (modified after Gorbunov et al., 1985).

bodies. Both occur discordantly and subconcordantly in the sulfide-bearing graphitic sediments of the Pilgujärvi Formation. In most cases the thicknesses of the ultramafic bodies range from 5 to 250 m. An exception to this is the 466-m-thick Pilgujärvi intrusion. Strike lengths of the ultramafic bodies range from 100 m to 6.5 km (Zak et al., 1982).

Figure 10b shows the Kaula deposit, which illustrates the common features observed in the Pechenga ores. A massive sulfide lense 1 to 10 m thick occurs at the base of the flow. The massive sulfides have also been mobilized by cataclastic deformation into the country-rock sedimentary units, and here the sulfides occur as matrix breccia sulfides (Fig. 6f). Overlying the massive sulfides is a 1- to 3-m-thick olivine cumulate with matrix sulfides and overlying this in turn is a thicker zone (30–100 m) of olivine cumulate containing disseminated sulfide. Finally there is a zone of ferropicrite 30 to 100 m thick at the top.

Sudbury

The 1.85 Ga (U/Pb; Krogh et al., 1984; Corfu and Lightfoot, 1996) Sudbury Igneous Complex straddles the Archean-Grenville contact in Ontario (Card et al., 1984; Fig. 11a). Nickel-copper ore deposits are found at the base of the intrusion and are associated with the radial and ring diorite dikes that are present around the intrusion (Fig. 11b).

There is now broad agreement that formation of the Sudbury Igneous Complex and many of the structures found in the Sudbury area are the result of shock waves from the explosion of a large meteor in the atmosphere (Dietz, 1964). The meteor is estimated to have been 10 km in diameter and the shock waves produced a transient crater 200 km in diameter (Grieve, 1994). Evidence for this model is the presence of fall-back breccia in the center of the structure (the Onaping Formation), the basin shape of the structure and upturned Huronian rocks around the margins (Dressler, 1984a, b), shatter cones and shock lamellae in quartz and feldspar (Dressler, 1984a, b; Pattison, 1979), abundant footwall breccia, and a pseudotachylite (the Sudbury breccia; French, 1967; Spray, 1995).

The shock waves from the meteor explosion are thought to have flash melted the crust to produce a large sheet of melt with an average composition close to that of the upper crust. This melt sheet then differentiated into the granophyre,

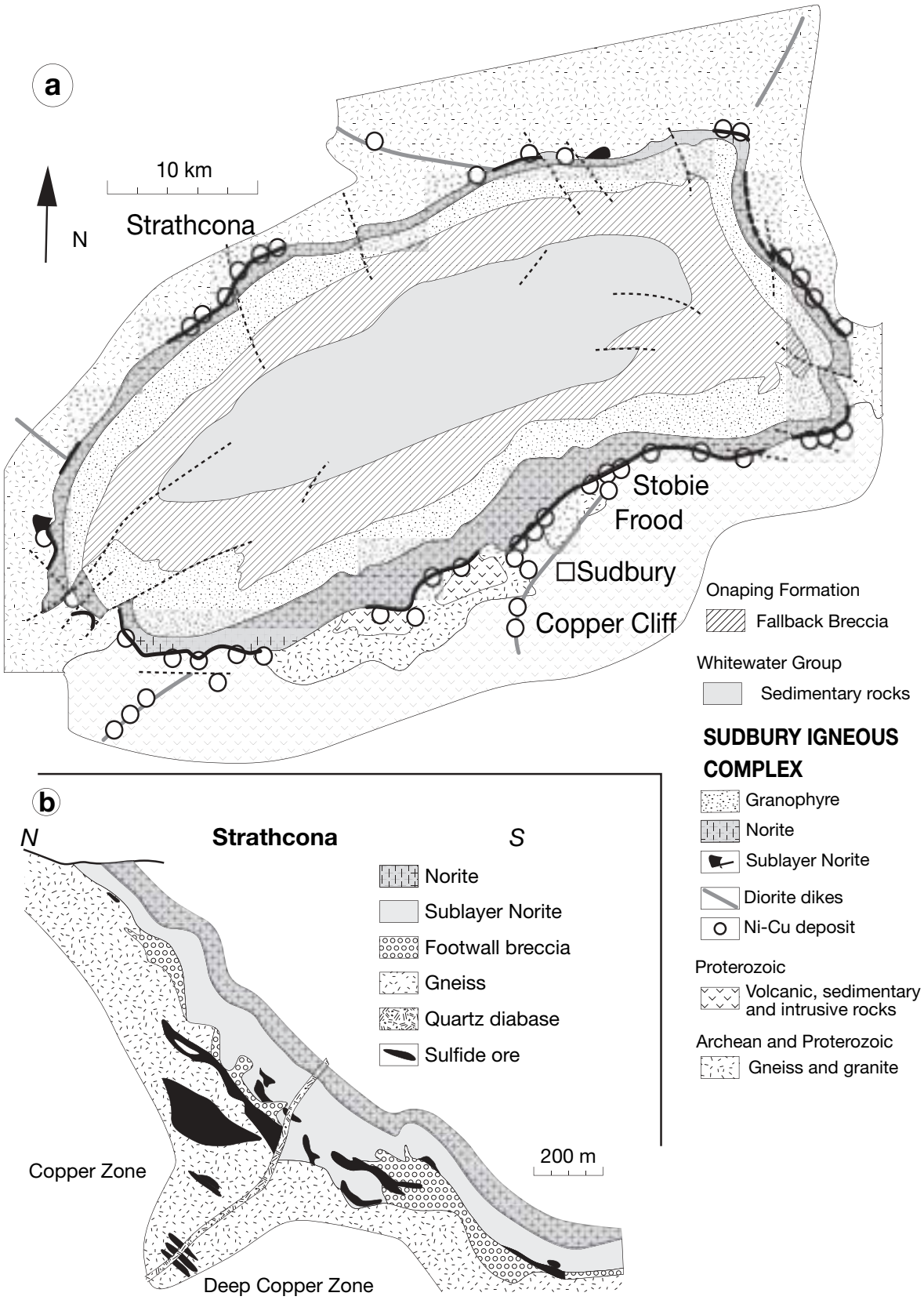


FIG. 11. a. Regional geology of Sudbury Igneous Complex (modified after Souch et al., 1969) b. Cross section of the Strathcona mine (modified after Li et al., 1983).

which forms approximately 60 percent of the complex, and leuconorite to norite, which form most of the remaining 40 percent of the complex (the norite is referred to as mafic norite, and the leuconorite is referred to as felsic norite in some publications). Around the edge of the complex are a number of embayments that are filled with an inclusion-rich norite which is referred to as the sublayer (Fig.11b). The inclusions consist of cognate xenoliths from the intrusion (Lightfoot, 1997a), exotic ultramafic clasts (Rae, 1975), and local country rock. In many cases the country rock adjacent to embayments is brecciated (footwall breccia). The clasts are angular to subrounded in a wide range of sizes. Dressler (1984a) reported shock metamorphic deformation in the clasts and granoblastic and granophryic textures in the matrix.

Some 50 percent of the mineral resources at Sudbury occur in the sublayer norite or the footwall breccia that is in contact with the sublayer. The sublayer norite contains disseminated sulfides, e.g., the hang-wall zone of Strathcona (Fig. 11b). Massive Ni-Cu sulfides occur toward the base of the sublayer and in the footwall breccia (Fig. 11b). Massive sulfides also occur in fractures immediately beneath the footwall breccia (Deep copper zone; Fig. 11b).

The final component of the Sudbury Igneous Complex is the quartz diorite dikes, known as offset dikes (Grant and Bite, 1984; Lightfoot et al., 1997a, b). These dikes are 50 to 100 m wide and extend for several kilometers into the country rocks. In many cases they follow zones of pseudotachylite (known as the Sudbury breccia). The dikes have a composition similar to the norites of the complex and are thought to represent injections of the differentiated impact melt into the country rocks. Forty-five percent of the Ni-Cu sulfide ore deposits are associated with the Frood, Stobie, and Copper Cliff dikes. The Ni sulfides take the form of massive sulfides both at the center and on the margins of the dikes and occur where the dikes widen.

Treatment of Whole-Rock Data from Ni Sulfide Deposits

Obiviously the concentrations of Ni, Cu, and PGE are important in determining the viability of a Ni sulfide deposit. But in addition to the absolute concentrations the ratio of the elements relative to each other and relative to sulfur are useful both to determine the petrogenesis of the rocks as well as to aid in exploration, Two methods used to interpret Ni, Cu, and PGE data; normalization to mantle and normalization to 100 percent sulfides are presented below. A third method which consists of interelement plots is presented after the section on petrogenesis.

Normalization to mantle

Most authors present chalcophile element data on a line graph where the metals have been divided by mantle or chondrite values. The order of the elements in Figure 12 is from compatible behavior on the left side (Ni, Os, Ir) to incompatible on the right side (Pd, Au, Cu). The purpose of these diagrams is to compare the distribution of these elements relative to each other. The choice of whether to normalize to chondrite or mantle values depends on the specific application of the diagram. As explained elsewhere (S-J. Barnes et al., 1988), during separation of the earth's core from the mantle, PGE partitioned preferentially into the Fe-Ni core, leaving the mantle depleted in PGE relative to Ni and Cu. Therefore, the mantle-derived magmas from which Ni deposits form tend to be depleted in PGE relative to Ni and Cu. Consequently, normalizing the data to chondrite values always produces a trough-shaped pattern in the normalized plot. The history of core separation is not useful in an exploration program, and thus we recommend normalizing to mantle rather than chondrite.

Nickel deposits are thought to form when a base metal sulfide liquid segregates from a silicate magma (e.g., Naldrett, 2004). The PGE have much higher partition coefficients between silicate and sulfide liquid than Ni or Cu (Table 4). Therefore, the first sulfide liquid to segregate from a magma will be rich in PGE and, if normalized to mantle values, will have normalized Ni values approximately in line with Os and Ir and normalized Pd values in line with Cu (e.g., Noril'sk; Fig.12a). The silicate liquid from which this sulfide liquid segregated will be PGE depleted and any sulfide liquid that subsequently forms from it will also have a PGE-depleted pattern (e.g., Voisey's Bay; Fig.12b). In order to avoid confusion between depletion due to core separation and depletion due to sulfide segregation we normalize data to mantle values (Table 5).

Recalculation to 100 percent sulfides

On mantle-normalized diagrams, metal values can be plotted as whole-rock values, but because most metals are assumed to be present in the sulfide fraction, the comparison of rocks with different sulfide contents requires recalculation of the metal abundance to 100 percent sulfide (i.e., the metal tenor of the sulfide). This procedure makes two assumptions: chalcophile metals are predominately hosted by sulfides, and S has not been added or removed from the samples by metamorphism or alteration. For Ni and Co in ultramafic rocks containing low modal percent sulfide, the first assumption is not justifiable because a substantial quantity of Ni and Co is present in olivine, e.g., in a dunite containing 1 percent sulfide and 90 percent olivine, only a small fraction of the Ni in the whole rock will be present in sulfide. Furthermore, rocks with low sulfide content are more vulnerable to S redistribution during weathering or metamorphism because the surface area to volume ratio of the sulfides is high. An example of this may be the disseminated Mt. Keith sulfides, which consist of millerite and pentlandite (Barnes and Hill, 2000). Therefore, the composition of the sulfides should not be recalculated for rocks containing <1 modal percent sulfides. Care should also be taken to ensure that data are both precise and accurate, especially where recalculations are being made for rocks with relatively low S abundances.

The logic behind the recalculation is that the sulfides represent the crystallized products of a base metal sulfide liquid that separated from silicate magma at magmatic temperatures (1,000°–1,199°C; Naldrett, 2004). Experimental work has shown that the first phase to crystallize from a sulfide liquid is an Fe-rich monosulfide solid solution (mss) and the remaining sulfide liquid is Ni and Cu rich (Kullerud et al., 1969; Ebel and Naldrett, 1997; Fig. 13a, b). When the temperature decreases sufficiently (<900°C), the Cu-rich liquid crystallizes as intermediate solid solution (iss). The partition coefficient of Ni into mss is dependent on temperature and f_{S_2} of

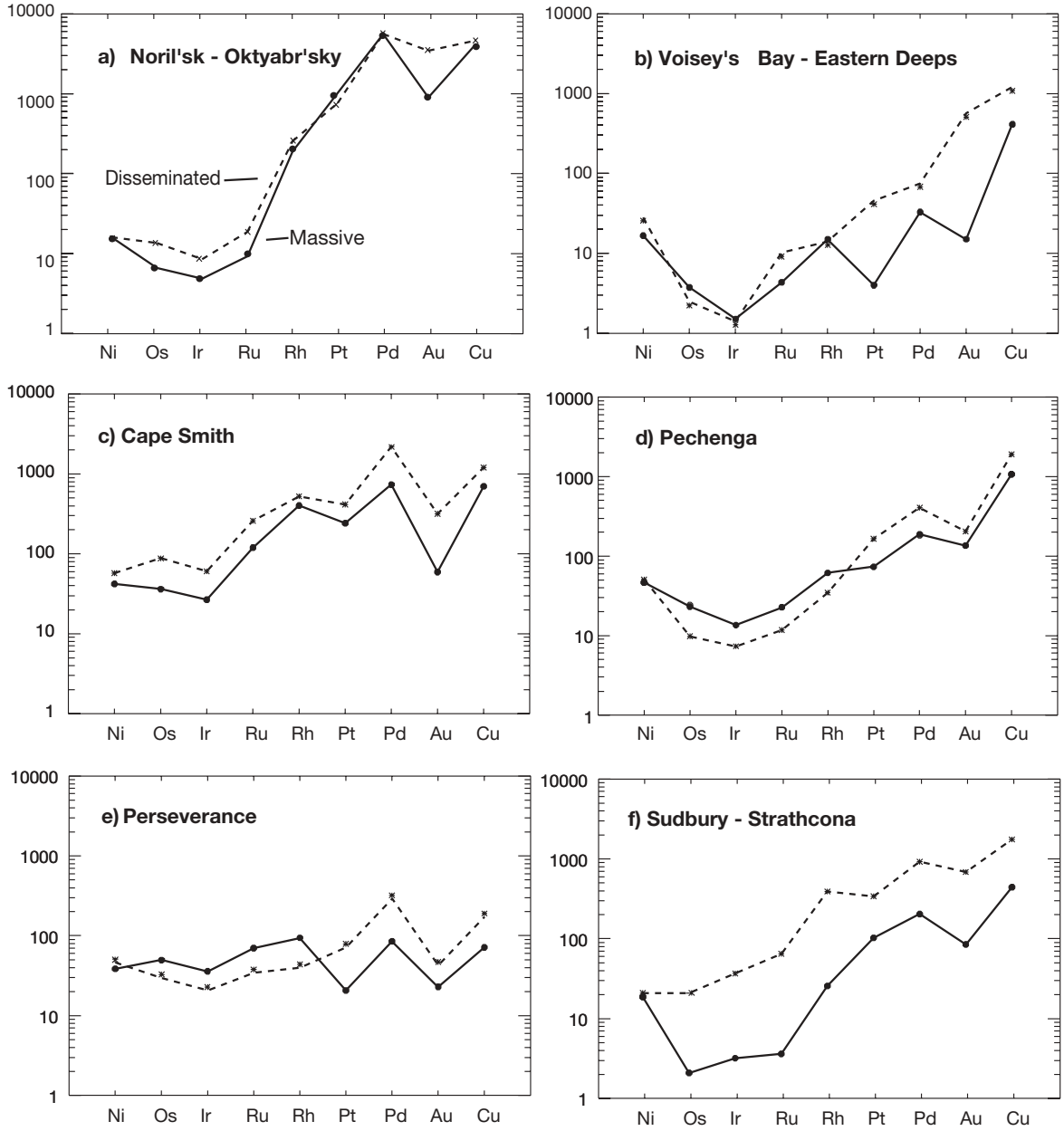


FIG. 12. Mantle-normalized plots for average disseminated and massive sulfides from (a) Noril'sk-Talnakh, (b) Voisey's Bay, (c) Cape Smith, (d) Pechenga, (e) Perseverance, and (f) Sudbury. Data sources in Table 1, and mantle normalization values in Table 5. Note that gabbronorite-hosted sulfides have steeper patterns than komatiitic- or picritic-hosted sulfides. Note also that in general disseminated sulfides (dashed lines) contain more PGE than massive sulfides and that the massive sulfides (solid lines) generally have flatter patterns than disseminated sulfides.

the system (Li et al., 1996; Barnes et al., 1997a; Makovicky, 2002) but in most cases it is in the 0.5 to 1.5 range (Table 4). Thus, Ni is found in both Fe- and Cu-rich ores. At temperatures <600°C, mss and iss are no longer stable (Fig. 13c-f). On the S-rich side of mss, the mss exsolves to pyrite and S-rich mss, and on the S-poor side it exsolves to pentlandite and S-poor mss. As the temperature decreases to <250°C the mss is no longer stable and pyrrhotite and pentlandite replace mss. Intermediate solid solution exsolves to form chalcopyrite and pyrrhotite (±pyrite, cubanite, mooihookite, talnakhite; Fig. 13d, f). During these exsolution processes, trace elements such as PGE, As, Sb, and Bi, which were originally present in the mss and iss, are exsolved and migrate toward the grain boundaries; these elements form PGM within and between the sulfide grains. Thus, the mineralogy observed in a magmatic sulfide under crustal conditions is essentially pyrrhotite, pentlandite, and chalcopyrite (±minor pyrite or cubanite) and various PGE-bearing antimonides, bismithides, arsenides, and tellurides. In rocks where the bulk of the sulfides are pyrrhotite, pentlandite, and chalcopyrite, the

TABLE 4. Partition Coefficients for the Metals

	Ni	Cu	Co	Os	Ir	Ru	Rh	Pt	Pd	Au	Ag	Re	Reference
						Partition coefficents between silicate liquid and							
Olivine	1.35–13.6		1.21–3.94										//earthref.org
Olivine				*	*	2.19*	1.4–2.6*	*	0.0047–0.014			<0.01	Brenan et al. (2003)
Olivine						0.23			0.12	0.12		0.017	Righter et al. (2004)
Orthopyroxene	0.6–1.4		1.12–2.08										//earthref.org
Clinopyroxene	2.6–4		1.32										//earthref.org
Chromite	3.5–6.8											<1.5	Sattari et al. (2002)
Spinel	10–20		4.7–8.3										//earthref.org
Spinel						22–25	78–90		0.2				Capobianco and Drake (1990)
Spinel						300–1200	130–430		0.4–1.2				Capobianco et al. (1994)
Cr spinel					5–132	76–1143	54–71		0.14	0.076		0.02–0.06	Righter et al. (2004)
Alloy				106–107	1012			1015	107	107			Borisov and Palme (2000)
Alloy	57–1607									1005–3543			Jana and Walker (1997)
Alloy	6000				300000					800000		40000	Wolf and Anders (1980)
Alloy	3100	80			100000					>40000			Kloeck et al. (1986)
Alloy		480–2273											Holzheid and Lodders (2001)
Sulfide liquid	315–424	913–1006											Francis (1990)
Sulfide liquid	810–1300			>31000	>50000	>12000	>140000	>18000	>92000			2100–18000	Sattari et al. (2002)
Sulfide liquid	410–580	250–313	17–24										Gaetani and Grove (1997)
Sulfide liquid	575–836	1383			14000				23000	15000–18000			Peach et al (1990)
Sulfide liquid	350–1070									110–1300			Jana and Walker (1997)
Sulfide liquid	257–274		61–80										Rajamani and Naldrett (1978)
Sulfide liquid		755–1303											Ripley et al. (2002) high fS_2
Sulfide liquid		480–969											Ripley et al. (2002) low fS_2
Sulfide liquid		380–1670											Holzheid and Lodders (2001)
Sulfide liquid					130000			9100	88000	1200			Stone et al. (1990)
Sulfide liquid				230	310000	2500	27000		55000	16000			Bezmen et al. (1994)
Sulfide liquid				3720	3180					3030			Crocket et al. (1992)
Sulfide liquid				2200–30000	1800–51000	2400–35000		1400–20000	2900–25000	900–3000			Fleet et al. (1999)
Sulfide liquid					35000				43000				Peach et al. (1994)
Sulfide liquid					450000				33000				Peach et al. (1994)
Sulfide liquid				48000								43	Roy-Barman et al. (1998)
Sulfide liquid								36000	25000				Helz and Rait (1988)
						Partition coefficents between sulfide liquid and							
Monosulfide	0.84	0.27		4.3	3.6	4.2	3.03	0.2	0.2	0.09			Fleet et al. (1993)
Monosulfide	0.36–0.8	0.2–0.25			3.4–11		1.17–3.0	0.05–0.13	0.09–0.2				Barnes et al. (1997a)
Monosulfide				2–6		3–8					0.5		Pededogova et al. (in press)
Monosulfide+	0.23				0.77	1	0.14	0.19	0.02				Fleet and Stone (1991)
Monosulfide+	0.18–0.36	0.17–0.2			0.08–1.4		0.4–0.8	0.01–0.05	0.01–0.07				Barnes et al. (1997a)
Monosulfide^	0.7–1.2	0.22–0.27			5–17		3.9–11	0.14–0.24	0.13–0.24				Barnes et al. (1997a)
Monosulfide	0.6–1.1	0.19–0.29			3.1–11.8	3–19	1.5–3.5	0.017–0.13	0.058–0.19				Ballhaus et al. (2001)
Monosulfide	0.54–0.74	0.26–0.28		3.8								2.5	Brenan (2002)
Alloy	0.10	0.06–0.16			135–324		1–6.5	11–130	0.04–0.15				Li et al. (1996)
Alloy	1.30			50–130	50–120	>30	30–110	90–300	0.9–2				Fleet and Stone (1991)
Alloy				12.9	11.6	10.0	8.0	8.1	2.6				Noddack et al. (1940)
Alloy	0.1–3				52–907			15–115		1.8–32			Jana and Walker (1997)
Alloy									0.4–2		0.01–0.21		Chabot and Drake (1997)
Alloy	1.4–2.24			341–5600	367–4180	41–164		40–300	0.7–1.47	1.3–3.16		323–4780	Fleet et al. (1999)

* = IPGE form nuggets at close to QFM + = S-undersaturated, not appropriate under crustal conditions, ^ = S-oversaturated, not appropriate under crustal conditions

Table 5. Concentration of Metals in Bulk Earth, Mantle, and Crust

	Ni (ppm)	Cu (ppm)	Co (ppm)	Os (ppb)	Ir (ppb)	Ru (ppb)	Rh (ppb)	Pt (ppb)	Pd (ppb)	Au (ppb)
Bulk earth	18220*	60*	880*	900*	900*	1300*	240*	1900*	1000*	160*
Primitive mantle	1960*	30*	105*	3.4^	3.4^	5^	0.95^	7^	4^	1^
Bulk crust	105+	75+	29+	0.1"	0.1+	~0.2"	~0.14"	~5"	~5"	3+
Upper continental crust	20+	25+	10+	~0.02"	0.02+	~0.04"	~0.02"	~2"	~2"	1.8+

* = McDonough and Sun (1995), ^ = Barnes and Maier (1999), + = Taylor and McLennan (1985), " = this work

concentration of an element in the sulfide may be calculated using the formula:

$$C_{(100\%\ sul)} = C_{wr}*100/(2.527*S + 0.3408*Cu + 0.4715*Ni), \quad (1)$$

where $C_{(100\%\ sul)}$ = concentration of an element in 100 percent sulfides; C_{wr} = concentration of the element in the whole rock; S, Cu, and Ni = concentration of these elements in the whole rock, in wt percent.

The validity of this calculation is very dependent on the mineralogy of the sulfides. The presence of abundant millerite, nicolite, bornite, and violarite suggests that the assemblage has been altered and should not be recalculated to 100 percent sulfide. However, for sulfide assemblages containing pyrrhotite, chalcopyrite, and pentlandite, the reliability of this calculation can be demonstrated by comparing calculated metal concentrations from sulfide ores with the composition of sulfide separates. For example, the composition of the observed sulfide separates from the Pechenga deposits matches the composition of the sulfides as recalculated from whole-rock values using equation (1) (see Table 2).

Table 2 also shows the average composition of sulfides for several Ni mining camps and deposits. Where available, the compositions of different textural types of sulfides are presented. However, at most localities there were very few matrix sulfide samples and the composition of the matrix and massive sulfides tend to overlap; therefore, averages are reported as massive plus matrix sulfide combined. Where the data is available, the massive and matrix sulfides may be further subdivided into those sulfides with Pd/Ir ratios less than disseminated sulfides and those with Pd/Ir ratios greater than disseminated sulfides. The sulfides with Pd/Ir ratios less than disseminated sulfides are generally Fe rich and Cu poor (Table 2). The sulfides with Pd/Ir ratios greater than disseminated sulfides are generally Fe poor and Cu rich (Table 2).

The sulfides associated with gabbronorites are much richer in Cu (3–30 wt %) and poorer in Ni (2–10 wt %) than sulfides associated with komatiites and picrites (0.1–2 wt % Cu; 8–12 wt % Ni). Within a particular ore deposit, Ni shows a much smaller variation in concentration than Cu and changes by a factor of two or less. Cobalt and Se also exhibit small variations in composition, with values of approximately 0.2 wt percent and 100 ppm, respectively, being common in both gabbronorite- and komatiitic-hosted sulfides. There are fewer data for As and Sb, and although they show a wide range in concentrations (0.1–100 ppm), individual deposits tend to exhibit more limited ranges; for example, Noril'sk has lower values than other deposits. The precious metal (PGE, Au, and Ag) concentrations are extremely variable; Pd concentrations for instance vary by three orders of magnitude. However, the precious metals do not show a preference for sulfides hosted by a particular rock type, and both high and low values are found in the gabbronorite- and komatiite-hosted sulfides. The main difference between gabbronorite-hosted sulfides and komatiitic sulfides is that komatiite-hosted sulfides are richer in Ir group (Os, Ir, Ru, Rh) and PGE (IPGE) than gabbronorite-hosted sulfides. Consequently, in the mantle-normalized plots, gabbronorite-hosted sulfides tend to have steep metal normalized plots (Fig. 12a, b, f), whereas picritic and komatiitic sulfides tend to have flatter patterns (Fig. 12c-e).

In most ore deposits the disseminated sulfides tend to have elevated metal tenors when compared to the massive sulfides. In particular, the disseminated sulfides tend to be richer in Pt, Pd, and Au than the average massive and matrix sulfides (Table 2; Fig. 12a-f). Breccia sulfides resemble the compositions of the massive and matrix sulfides (Table 2; Fig. 14e, f). In contrast, vein sulfides tend to be rich in Cu, Pd, and Pt (Table 2; Fig. 14a, b).

As mentioned above the massive and matrix sulfides vary in composition, with an Fe-rich portion enriched in Os, Ir, Ru, and Rh and a Cu-rich portion enriched in Pt, Pd, Au, and Ag. As a result, the Fe-rich sulfides tend to have flatter normalized metal patterns than the disseminated sulfides, whereas the Cu-rich sulfides have steeper patterns (Fig. 14a-d). Nickel and Co concentrations are similar to slightly higher in the Fe-rich sulfides than the Cu-rich sulfides.

In many cases S data are not available, and in some cases the rock has also undergone S mobility, thus normalization to 100 percent sulfides is not appropriate. In such cases, metal ratios of whole-rock values may be used to investigate and understand the genetic relationships between different types of sulfide mineralization and their host rocks. These will be discussed after the section on processes leading to the formation of Ni sulfide ores.

Processes Leading to Economic Concentrations of Ni-Cu-PGE

Melting

In general, the generation of mafic and ultramafic magmas typically takes place in the asthenospheric or lithospheric mantle, but contributions of partial or wholesale melts from the crust can also modify the composition of these mantle-derived magmas. The concentration of Ni, Cu, and PGE in

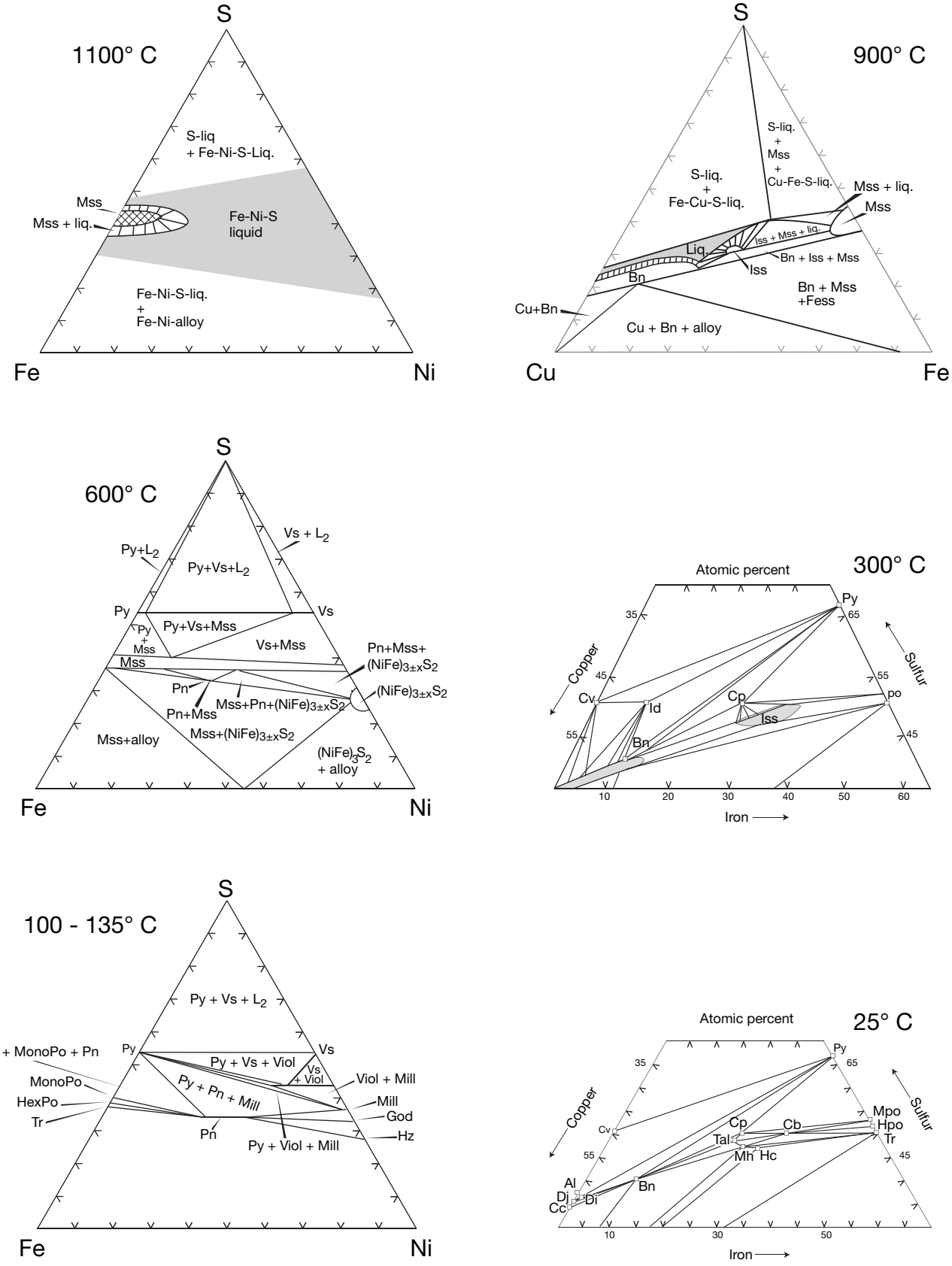


FIG. 13. Phase diagrams for the S-Fe-Ni and S-Fe-Cu system from Kullerud et al. (1969), Naldrett (2004), and Cabri et al. (1973), showing how the mineralogy of the system changes as temperature drops.

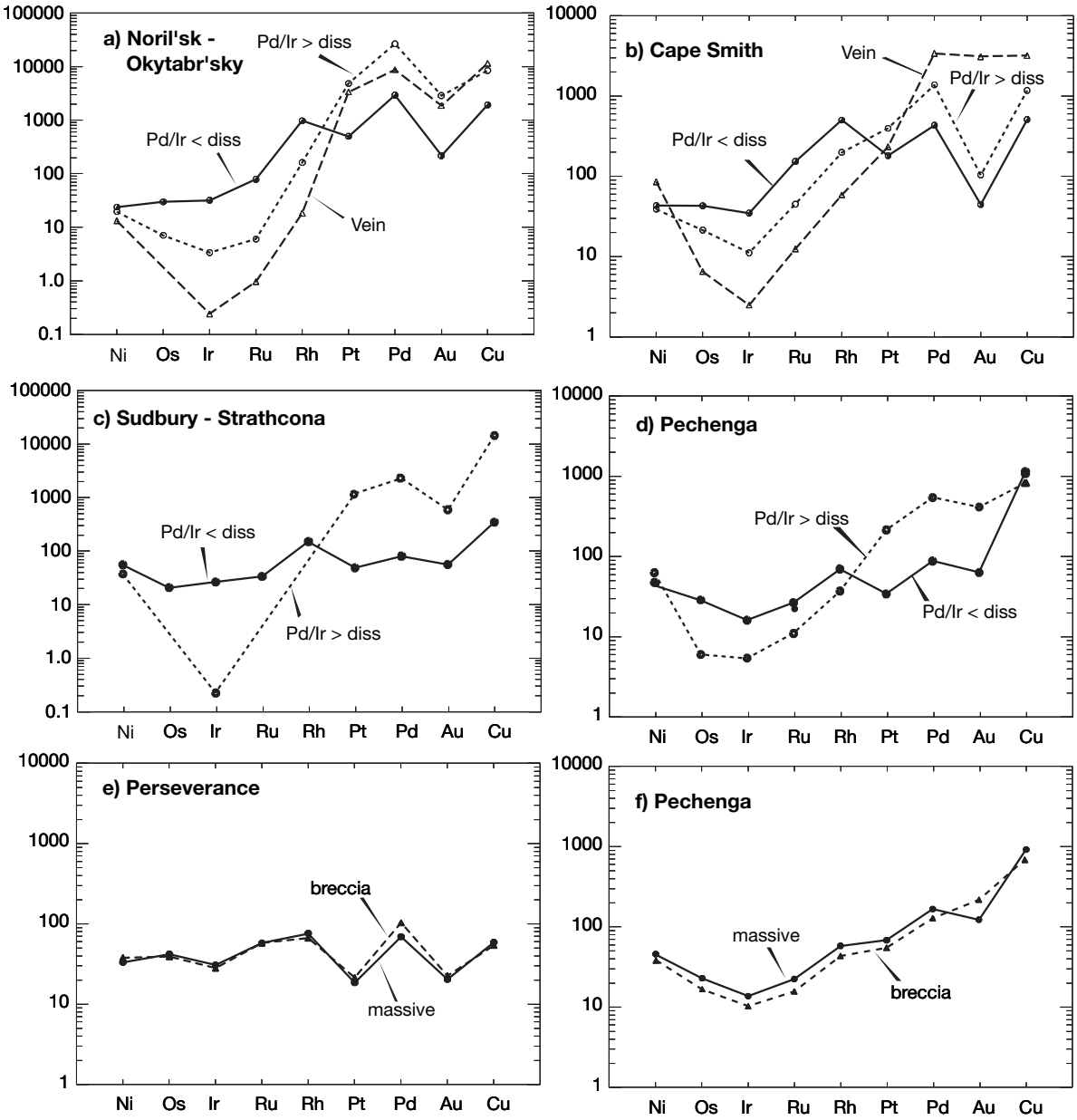


FIG. 14. Mantle-normalized plots of different types of sulfides. The massive and matrix sulfides from (a) Noril'sk-Talnalk, (b) Cape Smith, (c) Sudbury, and (d) Pechenga show variations in composition. Those with Pd/Ir ratio greater than disseminated ores (dashed lines) are enriched in Cu, Au, and Pt. Those with Pd/Ir ratio less than disseminated ores (solid line) are enriched in Os, Ir, Ru, and Rh. Sulfides found in veins (dashed lines with triangles) tend to resemble Cu-rich sulfides illustrated in (a) and (b). Breccia sulfides from Perseverance and Pechenga (dashed lines in (e) and (f)), resemble the average massive sulfides.

crustal and even in mantle rocks is very low when compared to bulk earth (Table 5) because these elements are siderophile (i.e., they prefer to form metals rather than oxides) and thus were concentrated in the core during the early history of the earth. Nickel ore deposits are 5 to 10 times richer in Ni and Co than the mantle and 100 to 200 times richer than in the crust (Table 5). The enrichment factor for the precious metals in ore deposits is typically much larger, approximately 1,000 times. Thus, from the point of view of forming a Ni ore deposit, the mantle would seem to be a more reasonable starting point than the crust.

The concentration of an element in the magma during batch partial melting (C_L) may be calculated from equation (2):

$$C_L = C_s/[F + D_B(1 - F)], \quad (2)$$

where Cs = concentration of the element in the source, F = degree of partial melting, and D_B = the bulk partition coefficient into the residuum, ΣDiXi + DjXj, Di = partition coefficient of the element into mineral i, and X = weight fraction of mineral i in the residuum. Using the metal contents established

for primary magmas (Table 6) and the degree of partial melting commonly estimated for these types of magmas, the bulk D required for each metal to approximate abundance levels in natural magmas can been calculated (Table 7).

The phase with the highest partition coefficient for Ni is sulfide liquid. However, the amount of sulfide in the mantle is very low (typically between 10–400 ppm with a mode of 200 ppm S, which is equivalent to 0.054 wt % sulfide; Lorand, 1993), so even if all of the sulfide remained in the mantle during partial melting, the sulfide contribution to the bulk partition coefficient of Ni would be very small (~0.1) when compared to the influence of olivine. Nickel has a moderate partition coefficient into olivine (1.5–13; Table 4), but olivine makes up about 70 wt percent of the mantle, so it is the main phase controlling Ni. Therefore, for magma to acquire the maximum amount of Ni, the degree of melting must be very high and a large contribution from melting of olivine is required. High degrees of partial melting result in high Ni contents in the magma. We can illustrate this empirically by looking at the Ni content of primary melts (Table 6). For example, komatiites are thought to have the highest degree of partial melting of all primary magma and they also have the highest Ni contents. In modeling the Ni content of primary melts it can be shown that the bulk D for Ni in the residuum must decrease from 10 at approximately 1 percent partial melting to 2 at 30 percent partial melting (Table 7). Olivine is the phase controlling the bulk D and the weight fraction of olivine in the residuum is not decreasing. This implies that the D for Ni into olivine decreases as the degree of partial melting increases. This is reasonable as experimental work shows that $D^{Ni/ol}$ decreases as temperature rises and the MgO content of the liquid increases (Hart and Davis, 1978).

In contrast to Ni, Cu, and Pd do not partition into olivine, and so their abundance in melts is dominantly controlled by sulfides (Table 4). The amount of sulfide that remains in the mantle during partial melting is controlled by the amount of S that the melt can dissolve. Experimental work (Wendlandt, 1982; Mavrogenes and O'Neil, 1999) indicates that at high

TABLE 6. Concentrations of the Metals in Primary Mantle Melts

	S (ppm)	Ni (ppm)	Cu (ppm)	Os ((ppb))	Ir (ppb)	Ru (ppb)	Rh (ppb)	Pt (ppb)	Pd (ppb)	Au (ppb)
Komatiite	740	1303	71	1.8	1.6	4.7	1.3	9.8	10.3	3.3
Picrite	796	498	86	2.10	0.76	2.36	0.76	10.86	9.54	5.22
MORB		157	87	0.01	0.05	0.16		3.08	2.10	0.84
OIB		173	112	0.38	0.20	0.30	0.36	8.58	7.00	4.35
Alkali basalt		365	71	0.39	0.20	0.43	0.33	3.11	1.95	1.49

Source Crocket (2002) and references therein, plus Maier et al. (2003 a, b), see also Arndt et al. (2005)

TABLE 7. Modeling of Partial Melting of the Mantle

Degree	1%	5%	10%	15%	20%	25%	30%	35%	40%
	Calculated concentration of metals in the melt using batch melting and attempting to match values in Table 6								
Ni (ppm)	202	233	274	328	400	500	833	1212	1250
Cu	87	112	114	116	99	80	67	57	50
Co	86	88	89	90	91	92	93	93	94
Os (ppb)	0.05	0.07	0.10	0.19	0.33	0.48	0.65	0.94	0.99
Ir	0.05	0.07	0.10	0.19	0.33	0.48	0.65	0.94	0.99
Ru	0.09	0.12	0.18	0.34	0.63	0.91	1.20	1.69	1.79
Rh	0.02	0.03	0.04	0.09	0.69	1.42	1.39	1.37	1.32
Pt	1.06	1.78	2.97	8.35	7.71	9.40	10.83	12.40	11.71
Pd	0.59	0.99	1.65	4.65	15.58	15.49	12.95	11.12	9.73
Au	1.81	2.88	3.80	5.37	4.75	3.89	3.27	2.81	2.46
	Bulk D used to calculate the metal concentrations in the melts								
Ni	10.01	9	8	7	6	5	3	2.00	2.00
Cu	0.22	0.14	0.08	0.03	0.00	0.00	0	0.00	0.00
Co	1.22	1.21	1.20	1.20	1.19	1.19	1.19	1.19	1.19
Os	66.70	52.60	38.58	21.25	12.63	9.10	7.08	5.05	5.05
Ir	66.70	52.60	38.58	21.25	12.63	9.10	7.08	5.05	5.05
Ru	54.40	42.70	31.27	17.20	9.70	7.00	5.50	4.00	4.00
Rh	41.60	32.30	23.47	12.65	1.48	0.56	0.55	0.53	0.53
Pt	6.66	4.08	2.51	0.81	0.89	0.66	0.50	0.33	0.33
Pd	6.66	4.08	2.51	0.81	0.06	0.00	0.00	0.00	0.00
Au	0.54	0.31	0.18	0.04	0.01	0.01	0.00	0.00	0.00
	Weight fraction of minerals in residuum based on bulk D								
Olivine	70	70	70	70	70	70	70	70	70
mss	0.041	0.033	0.02435	0.0135	0.001				
Sulfide liquid	0.014	0.007	0.0035						
Alloy					0.00025	0.0002	0.00015	0.0001	0.0001

pressures, mafic to ultramafic melts dissolve 500 to 1,000 ppm S. Assuming the mantle contains approximately 200 ppm S (Lorand, 1993), a minimum of 20 to 40 percent partial melting would be required to absorb all the sulfides in the mantle (e.g., MacLean, 1969; Barnes et al., 1985; Keays, 1995). If the sulfide phase that remains in the mantle at lower degrees of partial melting were sulfide liquid, then all primary basalts would have low Cu (30–60 ppm) and negligible Pd contents (<0.3 ppb), because the sulfide liquid would retain all the Pd and much of the Cu. As can be seen in Table 6, most primary mantle melts contain much higher concentrations of Cu and Pd than this (see also Arndt et al., 2005).

There is another reason why sulfide liquid cannot be the only phase controlling PGE behavior in the mantle. The partition coefficients for PGE between sulfide liquid and silicate magma are similar (Table 4). Thus, if sulfide liquid were the only phase controlling the PGE concentrations, then the ratio of PGE in primary melts should be the same as the ratio in the mantle, i.e., close to chondritic. However, most primary melts have Pd/Pt, Pd/Ir, Pd/Rh, Pd/Ru, and Pd/Os greater than mantle (Table 6). In general the bulk partition coefficient into the mantle decreases in the order Os ~ Ir > Ru > Rh > Pt > Pd (Barnes and Picard, 1993; Philipp et al. 2001; Momme et al., 2002; Maier et al., 2003a, b).

Barnes et al. (2001a), Brockrath et al. (2004), and Peregoedova et al. (2004) proposed a model to account for this. The model is based on experimental work on partitioning of PGE among sulfides at low pressure and on textural studies of mantle nodules (Lorand and Alard, 2001), which show that there are two types of sulfides in the mantle, Cu-rich iss that coats grain boundaries and Fe-rich mss as grains or inclusions in oxides and silicates. The mss is enriched in IPGE and the Cu-rich iss is rich in Pd. Pt is not present in either sulfide and is assumed to be present as Fe-Pt alloys. The model suggests that the Ni-Cu–bearing mss in the mantle undergoes incongruent melting to form Fe-rich mss, Cu-Pd sulfide liquid, and Fe-Pt alloys. The Pt-alloy and Fe-rich mss retain some IPGE and Pt in the mantle. The Cu-Pd sulfide droplets are entrained in the silicate melt and are carried by the silicate magma into the crust. These sulfide droplets will dissolve in the silicate melt as pressure drops (Mavrogenes and O'Neill, 1999), causing the PGE that were in the sulfide droplets to be released. Palladium and Au are sufficiently soluble to dissolve in the silicate melt, but according to the calculations of Borisov and Palme (2000), Pt, Ru, and Ir will not dissolve and these elements are removed from the magma as Fe-PGE alloys, thereby further depleting the magma in IPGE and Pt. The weakness of the model is that it assumes that mss will melt incongruently under mantle conditions and that sulfide droplets could be transported from the mantle.

Regardless, not everyone is convinced that sulfides are the phase controlling the fractionation of PGE. Two common phases found in the mantle, olivine and spinel, may be important. Brenan et al. (2003) has shown that Rh and Ru partition into olivine, whereas Pd does not. Capobianco and Drake (1990), Capobianco et al. (1994), and more recently Righter et al. (2004) showed that Ru and Rh are incorporated into spinel but Pd is not (Table 4). In both cases, by analogy it could be argued that Os and Ir should also be accommodated in olivine or spinel and hence Os, Ir, Ru, and Rh would be compatible during partial melting. Platinum would be expected to behave in a similar manner to Pd so these minerals will not separate Pt and Pd. Thus, in order to retain Pt in the mantle in preference to Pd, a Fe-Pt alloy would be required. Some reservation should be exercised in applying these experiments to mantle conditions. The experiments on PGE partitioning into spinel and olivine, carried out at an f_{O_2} which approximates natural conditions (FMQ ±1), were plagued with "nugget effects." Reproducible results were obtained at higher f_{O_2}, but in this case the oxidation states of the metals may be higher than that observed in natural systems. Nevertheless, a model using a Pt-Fe alloy and olivine or spinel to retain the IPGE and Pt during partial melting remains possible.

Continuing with the modeling we have assumed (as discussed above) that the residuum contains a small quantity of mss until all the S is dissolved into the silicate magma (Table 7; Fig. 15). Copper concentrations in the melt increase until 15 percent partial melting and then decrease (Fig. 15). Palladium concentrations also increase from 0.5 ppb in rocks formed at the lowest degree of partial melting to 15 ppb at 20 percent partial melting, at which point there are no sulfides left in the mantle (Table 7; Fig. 15). Iron-rich mss concentrates Os, Ir, Ru, and Rh. At <20 percent partial melting all of these metals are only present in primary melts at very low concentrations (Table 6). These concentrations can be modeled assuming mss is a residual phase. If no other phase accepted these elements, once all the sulfides are consumed at

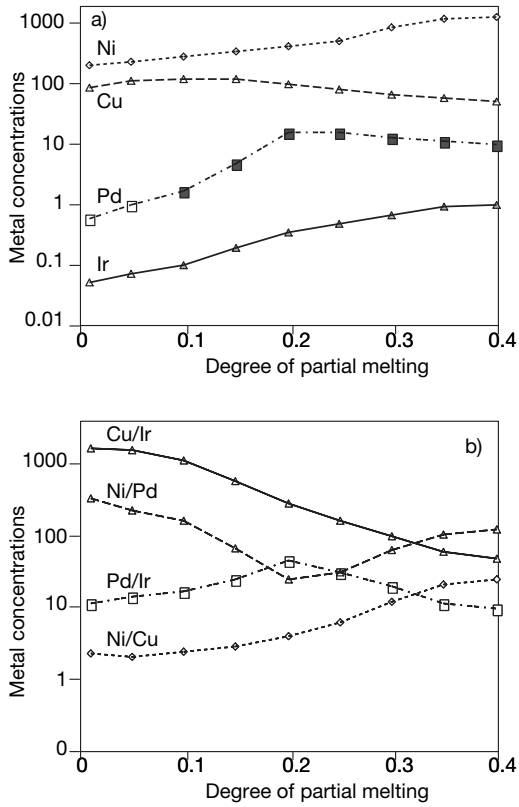


FIG. 15. Model of changes in (a) metal concentrations and (b) metal ratios in the magma versus the degree of partial melting, assuming the PGE concentrations are controlled by a combination of monosulfide solid solution (mss) and PGE alloys. Details of the modeling are shown in Table 7.

20 percent partial melting, then the concentrations should peak at approximately 5 times primitive mantle values, followed by a decline in a manner similar to Pd. However, at approximately 20 percent partial melting (e.g., the degree of melting appropriate for picritic basalts), the Ir concentrations are only one-fifth of primitive mantle, and Pt concentrations are only 1.5 times mantle. To model this we have allowed for a small amount of Fe alloy in the residuum. Assuming a small quantity of alloy is present above 20 percent partial melting, the composition of primary basalts and komatiites can be modeled (Table 7; Fig. 15).

As outlined above, the phases controlling the PGE remain open to debate. The model presented above used a combination of olivine, mss, sulfide liquid, and alloy. It may be that mss is not a relevant phase and that the distribution of PGE is controlled by a combination of spinel or olivine and alloy, but this will not change the bulk D listed in Table 7 required to obtain the observed metal concentrations.

The significant point of this discussion is that a high degree of partial melting of the mantle is favorable to obtain a silicate liquid that is rich in Ni and PGE. This liquid could subsequently segregate sulfides that are rich in these metals. An additional point is that if a large deposit is to form, then a large quantity of mantle should undergo this high degree of partial melting. The tectonomagmatic conditions favoring this type of melting are typically associated with mantle plume events where large volumes of magma are generated. The stem of plume may be the locus above which magmas are erupted or emplaced from domains that have undergone the highest degrees of partial melting (Fig. 16b).

Turning to the case of the Sudbury Ni ores, the rocks of the Sudbury Igneous Complex have an overwhelming major and trace element signature, plus isotopic ratios, that indicates they formed from the upper crust (e.g., Lightfoot et al., 2001). Although a contribution of mantle-derived magma can not be ruled out, there is no geologic evidence to indicate that such a contribution is required (Lightfoot et al., 1997a). Therefore, a major problem at Sudbury is to explain the association of the largest known concentrations of Ni ore deposits in the world with large volumes of crustal melt. The bulk continental crust has the composition of an andesite (Taylor and McLennan, 1985), similar in composition to quartz diorite dikes found at Sudbury. Many authors (e.g., Golightly, 1994) suggested that the Ni sulfides segregated from a liquid of this composition. Assuming that the melt was similar to bulk crust, it would have contained ~105 ppm Ni and ~ 75 ppm Cu (Table 5). As will be outlined in the section on sulfide saturation, provided there was sufficient silicate magma available, the metals would have become enriched in the sulfide fraction by a factor equal to the partition coefficient. For Ni in the Sudbury diorite (an intermediate magma) this would have led to an enrichment factor of 300 to 500 (Table 4), and thus the Ni content of the sulfide liquid could potentially be 3 to 5 percent, which is similar to the sulfides in the disseminated sulfides at Sudbury (Table 2). The important points in the melting stage are that a very large quantity of melt was produced liberating a large amount of Ni from silicates, even though the Ni concentration in the melt was relatively low; and, although the temperature of the melt was very high, sulfide saturation was achieved shortly after melt-sheet generation, and thus there was a long time for sulfides to collect Ni from the melt (Keays and Lightfoot, 2004; Li and Ripley, in press).

Transport of the melt

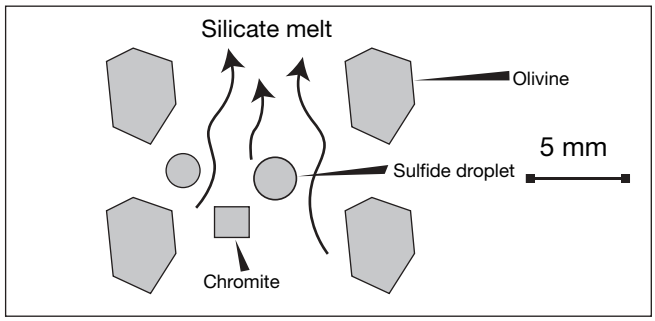
A key requirement to form typical Ni sulfide ore, as opposed to the Sudbury ores, is that melts formed in the mantle must be efficiently transported into the crust with a minimum degree of olivine fractionation and sulfide segregation. If olivine were removed from the melt, the Ni content of the melt would decrease. For example, assuming Rayleigh fractionation the concentration of an element in the fractionated liquid (C_f) may be calculated using equation (3).

$$C_f = C_i\, F^{(D_B^{-1})}, \qquad (3)$$

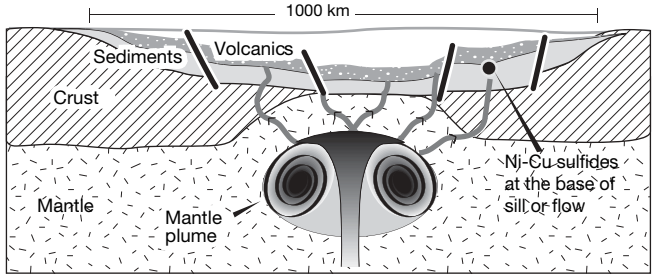
where C_i = concentration of the element in the initial liquid, F = the weight fraction liquid remaining, and D_B = bulk partition coefficient as defined for equation (2). If olivine were the only phase in the liquidus, and assuming a partition coefficient for Ni between olivine and silicate melt of 4, after 5 percent crystal fractionation (F = 0.95) the Ni concentration in the magma would be reduced by a factor of 0.85 (Fig. 17). If the magma became saturated with base metal sulfide liquid and this liquid were to settle out the magma, then other metals in addition to Ni would be depleted in the magma. For a picritic magma, if olivine and sulfides were removed in cotectic proportions, then approximately 99.1 olivine and 0.9 percent sulfide liquid would be removed. The depletion factor for Ni would rise from 0.85 (for olivine-only fractionation) to 0.77 (for olivine plus sulfide) at 5 percent fractionation, but more importantly the depletion factors for the PGE would be much higher because of their very high partition coefficients into sulfides. For the PGE, the depletion factor would be between 0.0062, assuming a relatively low partition coefficient for PGE between sulfide and silicate liquid of 10,000, and 10^{-9}, assuming a relatively high $D^{PGE/sul\ liq}$ of 40,000. PGE are extremely sensitive to the removal of sulfides and as little as 2 percent crystallization with sulfide in cotectic proportions would lower the PGE contents by a factor of 0.003 to 0.13 (Fig. 17). This is thought to be the reason for the exceptionally low PGE abundances in basaltic magmas overlying the Cape Smith and Noril'sk deposits (Maier et al., 1998; Barnes and Maier, 1999; Lightfoot and Keays, 2005) and the pronounced depletion in the upper noritic rocks of the Sudbury Igneous Complex (Keays and Lightfoot, 2004). The PGE depletion is important because this provides a strong indication that rocks that are genetically linked to the Ni sulfide ores record evidence of metal depletion due to sulfide formation.

A small amount of crystallization of olivine or sulfides will not lower the Ni content of the magma appreciably, and a viable Ni deposit may form from this magma. However, removal of sulfides will sharply deplete the magma in PGE and mildly deplete it in Cu (Fig. 17). Any sulfide liquid that forms subsequently will be depleted in PGE relative to Ni and Cu. Prior removal of sulfides may be one of the main reasons why some Ni sulfide deposits have low PGE contents compared to others. Compare for example the disseminated sulfide compositions at Noril'sk and Voisey's Bay (Table 3; Fig. 12a, b). In both cases the Ni sulfide ores are hosted by mafic rocks and their sulfides have similar Ni contents. Yet the

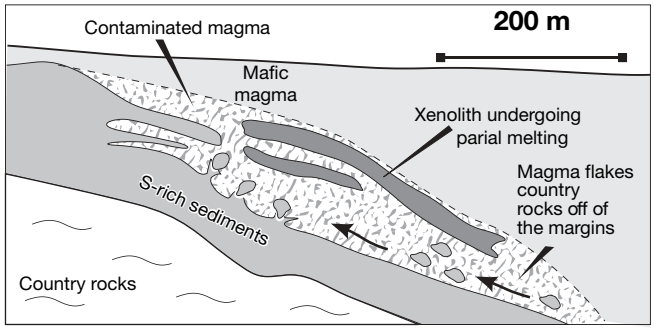
a) Partial melting of mantle, high degree of partial melting needed to release Ni from olivine



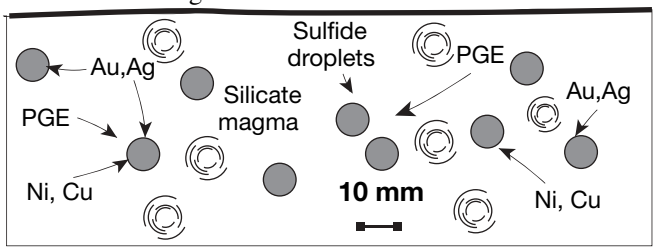
b) Transport of magma into the crust



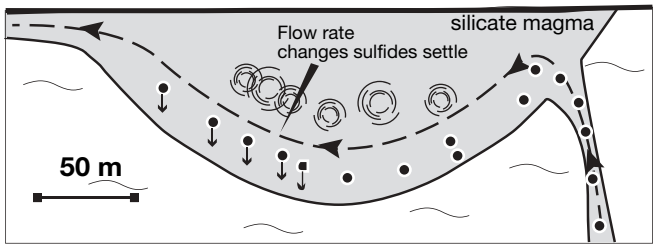
c) Contamination of the magma brings about sulfide saturation



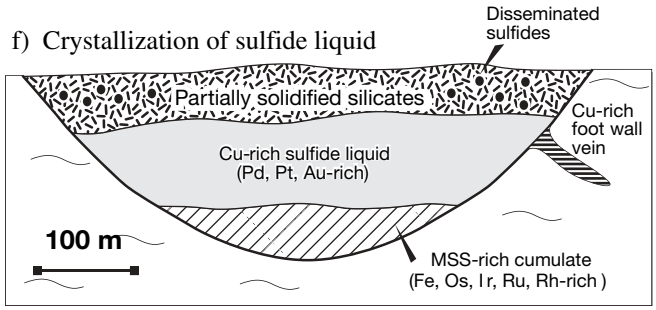
d) Collection of the metals by sulfide liquid Vigorous convection raises silicate to sulfide liquid ratio resulting in Ni and PGE rich ores



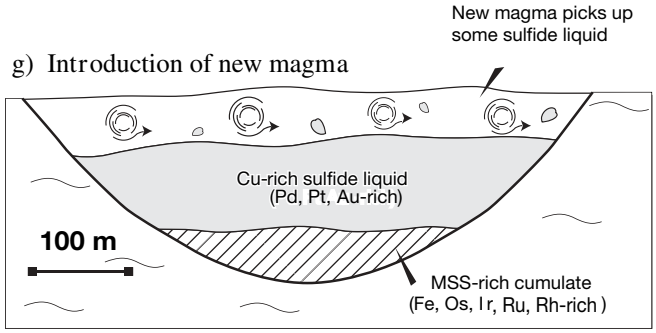
e) Collection of the sulfides in some structural trap



f) Crystallization of sulfide liquid



g) Introduction of new magma



h) Deformation of sulfides to form brecciated sulfides

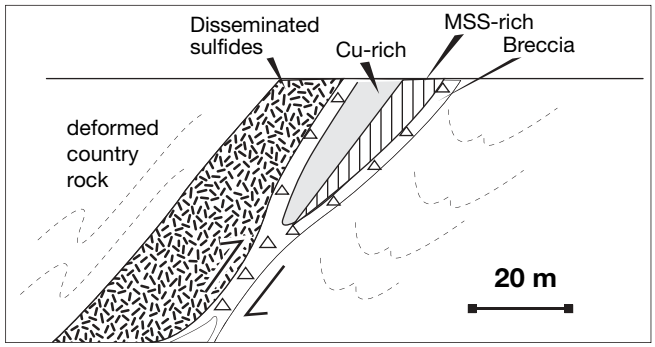


FIG. 16. Cartoon outlining the processes that lead to the formation of a Ni sulfide ore deposit. a. The mantle melts to release Ni from olivine and PGE from sulfides. b. Magma is transferred to the crust along crust penetrating faults. c. Sulfur is added to the magma from sediments to bring about saturation of a sulfide liquid. d. The sulfide droplets assimilate chalcophile metals. e. The droplets are transported by the magma until the magma flow slows such that they collect at the base of the intrusion or flow. f. The sulfide liquid undergoes crystal fractionation to produce an mss cumulate and a Cu-rich liquid that can be injected into the footwall. g. In some cases there may be a new injection of magma and the Cu sulfide liquid may be entrained and moved to a new site collection site. h. Deformation concentrates in the incompetent sulfides, resulting in sulfides being displaced from their parent body, possibly as breccias.

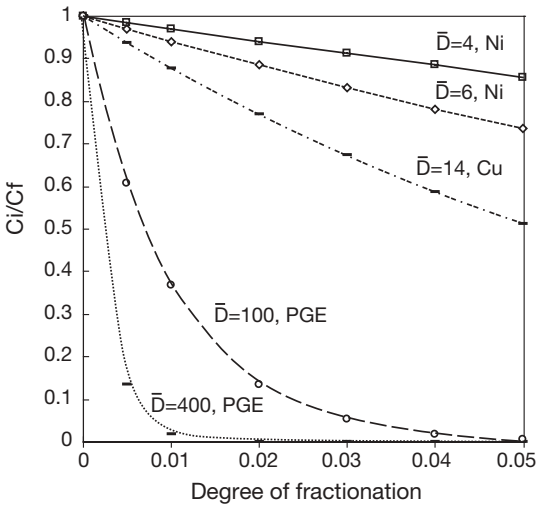


FIG. 17. Model of changes in metal concentrations in a silicate melt during crystal fractionation. Two curves are shown for Ni, one assuming no sulfide extraction (D = 4), and one assuming that olivine and sulfides have been extracted from the melt in approximately cotectic proportions (D = 6). Note the addition of sulfide extraction does not change the Ni content in the melt significantly. Two possible curves are shown for PGE, one assuming the $D^{PGE/sul}$ is 10,000 (bulk D = 100), and one assuming $D^{PGE/sul}$ = 40,000 (bulk D = 400). Note that even a small amount of sulfide extraction dramatically lowers the PGE content of the melt.

Noril'sk sulfides contain two orders of magnitude more Pd than the Voisey's Bay sulfides (Table 3; Fig.12a, b). Likewise, both the Cape Smith and Pechenga sulfides are hosted by ultramafic flows and yet the Cape Smith sulfides are much richer in Pd than the Pechenga sulfides (Table 3; Fig. 12d, e). It is not only the PGE content that is different. The ratios Ni/Ir and Cu/Pd are greater than mantle for the Pechenga and Voisey's Bay deposits, and consequently their mantle-normalized patterns have trough shapes (Fig. 12b, e).

Conditions favoring direct transport of the melt to the site of emplacement will ensure that the magma arrives with the minimum of olivine crystallization and sulfide segregation. A plume intersecting a rift is an ideal site for emplacement since the continental crust is thin in the rift, and the magma can efficiently travel along well-defined conduits that follow major crustal structures. This is the type of setting proposed at Noril'sk-Talnakh, Cape Smith, Pechenga, and Duluth (Fig. 16c). In the case of Voisey's Bay, the magma was emplaced close to the suture between the Churchill and Nain provinces. The suture probably did not provide as easy access for the magma as the normal faults of a rift zone, and hence the magma may have paused en route to surface and segregated PGE-rich sulfides at depth (Lightfoot and Naldrett, 1999). The poor access of magmas through the crust may explain the presence of small PGE-depleted Ni occurrences in small intrusions of the Grenville, Sveconorwegian, and Svecofennian provinces (S-J.Barnes et al., 1988; Papunen, 1989).

Factors leading to base metal sulfide liquid saturation.

Once the magma has been emplaced into the crust it must become saturated in a base metal sulfide liquid (dominantly FeS) in order for it to have the potential to form a Ni sulfide deposit. It is this sulfide liquid that collects the metals. Li and Ripley (in press) recently reviewed the published work on the factors leading to the saturation of magmas in an Fe sulfide liquid. In summary, the factors that affect the saturation of silicate magma in Fe sulfide liquid include the following: (1) a rise in pressure, (2) a fall in temperature, (3) a change in magma composition (in particular a drop in Fe content or an increase in SiO_2, $Na_2O + K_2O$, or MgO), (4) an increase in f_{O_2}, and (5) a decrease in f_{S_2}. Li and Ripley (in press) developed an empirical equation to estimate the S concentration of a magma saturated in sulfide liquid,

$$\begin{aligned} ln X_s = {} & 1.229 - 0.74^*(10^4/T) - \\ & 0.021^*P - 6.166^*X_{SiO_2} - 9.153^*X_{(Na_2O + K_2O)} \\ & - 1.914^*X_{MgO} + 6.594^*X_{FeO} - 0.311^*ln X_{FeO}, \end{aligned} \quad (4)$$

where X = the mole fraction of an element, T = temperature in Kelvin, P = pressure in kbars. Li and Ripley (in press) did not find it necessary to include terms for f_{O_2} and f_{S_2} because in terrestrial mafic magmas, f_{O_2} controls the f_{S_2}, and f_{O_2} is in turn controlled by FeO and temperature. Thus, by including FeO and temperature in equation (4) the effects of changes in f_{O_2} and f_{S_2} are taken into account.

An important point is that S solubility decreases with increased pressure (Mavrogenes and O'Neil, 1999). Thus, although a primary magma might be saturated in base metal sulfide liquid when it formed in the mantle, as the magma rises and the pressure decreases the sulfide liquid will tend to dissolve. For example, using equation (4) the amount of S the Cape Smith komatiitic basalts could dissolve at 30 kbars, would be ~1,300 ppm (assuming a liquidus temperature of ~1,500°C at 30 kbars), whereas at 1 kbar the same magma could dissolve ~1,800 ppm S (assuming a liquidus temperature of 1,370°C). Therefore, in a closed system approximately 40 percent crystal fractionation would be required before the magmas would become saturated in sulfide liquid. Fractionation of 40 wt percent olivine would reduce the Ni content of the magma by ~0.2 (i.e., from ~500–100 ppm) and hence very little Ni would be available to form a Ni sulfide.

Thus, in order to bring about sulfide saturation of primary magmas, some process is required, such as cooling of the magma or change in composition of the magma. In a crystallizing magma the solubility of S should decrease as the temperature decreases. However, in the early stages of crystallization of an ultramafic magma, this decrease in S solubility may be offset by changes in the magma composition. If there is an increase in the FeO content of the silicate liquid, the S solubility of the magma may increase. In contrast, in the later stages, Fe-rich silicates and oxides crystallize and the Fe content of the magma will decrease, resulting in a decrease in S solubility; in this case a sulfide liquid may form in association with the oxide. This will not lead to a Ni sulfide deposit because the magma would be depleted in Ni by the time sulfide saturation is achieved.

A mechanism commonly proposed to achieve saturation is assimilation of crustal rocks by the primary magma (e.g., Grinenko, 1985; Theriault and Barnes, 1998; Lesher and Burnham, 2001; Ripley and Li, 2003). The common association of the S-bearing crustal rocks with Ni sulfide deposits suggests that the former are important to the formation of the

deposits. This is further supported by the S isotope composition of the ores that indicate the S was derived largely from the country rock (e.g., Noril'sk and Pechenga; Fig. 18). Assimilation of these types of crustal rocks will lower the temperature of the magma and increase the S concentrations, thus bringing about S saturation. In the Duluth Complex there are convincing examples of in situ assimilation of black shale, leading to local sulfide saturation (Ripley and Al-Jassar, 1987; Theriault and Barnes, 1998). The mechanism for this assimilation appears to have involved stoping of country rock to become xenoliths in the magma chamber (Fig. 16c). These xenoliths are subsequently heated by magma, causing partial melting, formation of granitic melt, and release of S to the mafic melt. In addition to lowering the temperature of the magma and adding S, mixing of the granitic melt into the basaltic magma would lower the FeO and raise the SiO_2, Na_2O, and K_2O content of the melt, thus aiding sulfide saturation (see eq. 4).

It has also been suggested that in some cases S could be transported to the magma from the country rock to the magma as a gas (Barnes et al., 1997b; Ripley, 1981; Grinenko, 1985). Baker et al. (2001) have shown experimentally that S will migrate through graphite to an S-undersaturated basalt. At present it is not clear whether this occurs in natural systems; however, Grinenko (1985) strongly favored S transfer by a gas phase during formation of the Noril'sk-Talakh ores.

Sulfur-rich sedimentary rocks are not always present in the immediate country rocks of a Ni sulfide deposit. For example, the Eastern Deeps and Ovoid Ni sulfides ores at Voisey's Bay occur in orthogneiss and granite. Ripley et al. (2002b) used O and S isotope data to suggest that the S in the deposits was derived from both the paragneiss that is located at the west end of the deposit and the orthogneiss at the eastern end of the deposit (Fig. 8b).

Collection of metals by sulfides

Campbell and Naldrett (1979) showed that in a closed system the concentration of a metal in a sulfide liquid (C_S) is controlled by the concentration of the metal in the silicate liquid (C_L), the partition coefficient between the sulfide and silicate liquids (D), and the volume of silicate magma from which the sulfide collects the metal, expressed as R (ratio of silicate to sulfide liquid).

$$C_S = C_L D(R + 1)/(R + D). \quad (5)$$

Brügmann et al. (1993) suggested that in many cases, such as where sulfide droplets sink through a magma column or

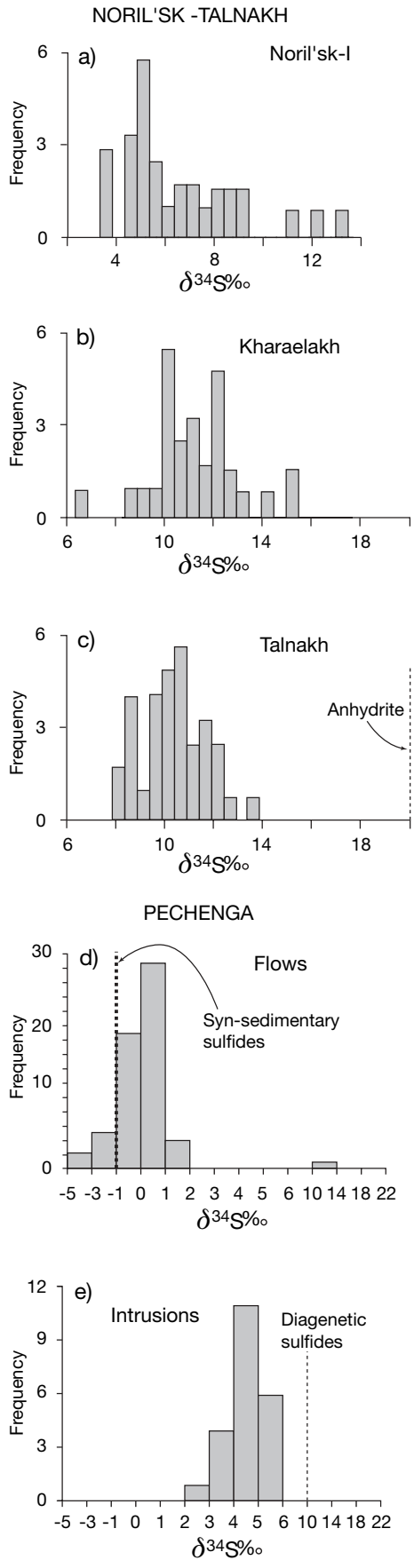


FIG. 18. S isotope compositions for Noril'sk-Talnakh (Grinenko, 1985) and Pechenga (Barnes et al., 2001b) Ni sulfide ores. The Noril'sk-Talnakh ores are enriched in ^{34}S relative to mantle-derived rocks, which have $\delta^{34}S$ values close to zero per mil. The ^{34}S is believed to have been contributed to the magma from anhydrite in the country rocks, with $\delta^{34}S$ values of 20 per mil. The sulfides associated with intrusions from Pechenga are also enriched in ^{34}S, with most $\delta^{34}S$ values in the 3 to 6 per mil range. The ^{34}S is believed to have been derived from the diagenetic sulfides in black shales of the country rock. The sulfides from flows that erupted onto unconsolidated black shales at Pechenga have low $\delta^{34}S$ values, similar to mantle values. The synsedimentary sulfides of the black shales have $\delta^{34}S$ values close to zero per mil, and thus the Ni sulfides do not have a distinctive crustal signature.

where the silicate magma is replenished, a variation of the zone-refining equation would be more appropriate to model the sulfide composition,

$$C_S = C_l(D - (D - 1)e^{-(1/DN)}, \quad (6)$$

where N = number of volumes of magma with which the sulfide liquid interacted.

The qualitative results are similar using either equation (5) or (6). As originally pointed out by Campbell and Barnes (1984), when R or N is greater than 10 times D, the enrichment factor (C_S/C_L) in the sulfides approaches D and where R is less than 10 times D, the enrichment factor is approximately R (Fig. 19). The partition coefficient of Ni between silicate and sulfide liquid varies from 100 for komatiitic liquids to 300 for basaltic liquids. Thus, in komatiites an R or N factor of 1,000 is required to achieve maximum Ni enrichment, and an R or N factor of 3,000 is needed to achieve maximum Ni enrichment in basaltic systems.

The difference in the partition coefficient of Pd and Cu into a sulfide liquid may be used to deduce the volume of magma from which a sulfide segregated (Barnes et al., 1993). Assuming a partition coefficient for Cu of 1,000 and for Pd of 30,000, for R < 100, Cu and Pd will be enriched in the liquid equally and the Cu/Pd ratio will be the same in the silicate and sulfide liquid (Fig. 19). For R > 100, Pd will be enriched more than Cu, and the mantle-normalized metal patterns will show an enrichment in Pd relative to Cu (e.g., Noril'sk; Fig.12a).

In order to make PGE-rich sulfide, the sulfide liquid must interact with a very large volume of silicate magma. As mentioned above, maximum Ni enrichment is achieved at R factors of 1,000 to 3,000, in contrast to maximum PGE enrichments that require R factors of >10,000. In order to achieve the degree of enrichment observed in the Noril'sk disseminated sulfides, an R factor of 1,000 to 10,000 would be required (Fig. 20). This implies an extremely dynamic system.

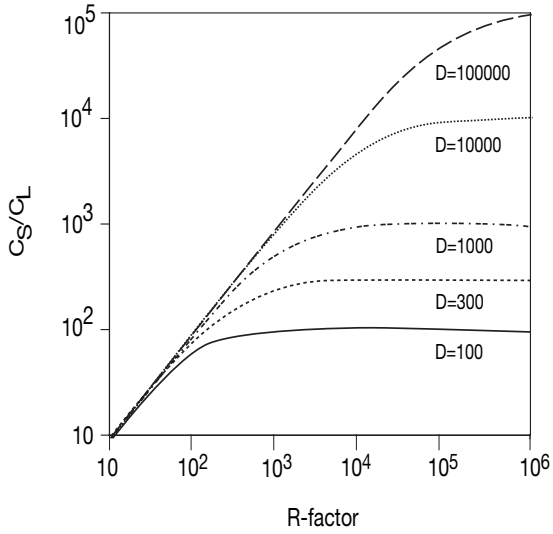


FIG. 19. Model of metal enrichment (C_S/C_L) during sulfide collection vs. the R factor (the ratio of silicate to sulfide liquid). Curves shown for a range of partition coefficients (see text for discussion).

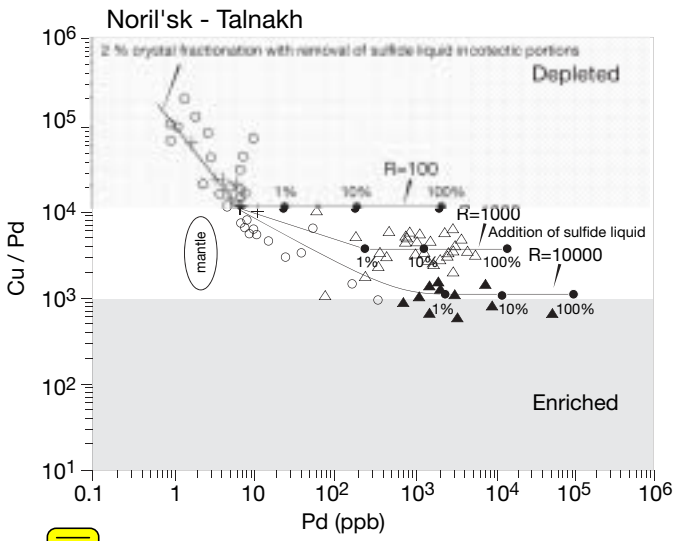


FIG. 20. Finite element model of suspension of a sulfide droplet above an embayment, allowing the sulfide droplet to become enriched in metals (based on Rice and Moore, 2001).

In the case of Noril'sk-Talnakh, the intrusions that contained the sulfides can be thought of as conduits through which many pulses of magma may have been transported. In the case of komatiite ores such as Kambalda, it has been argued that the sulfide droplets were transported by the komatiite flow and during transport the suspended sulfide droplets interacted with a large volume of silicate magma to enrich the sulfides in Ni and PGE (e.g., Lesher and Keays, 2002, and references therein). Rice and Moore (2001) presented an elegant model to show how sulfide droplets could be kept in suspension above an embayment in the footwall by the turbulence created in the komatiite magma, due to an uneven footwall topography (Fig. 21). For the Voisey's Bay deposits, Li and Naldrett (1999) and Lightfoot and Naldrett (1999) argued that after the sulfides formed at a deeper level, the sulfide droplets were transported through the dike to Eastern Deeps, and in the process the sulfides interacted with a large volume of magma.

Collection of sulfides:
Structural traps in which sulfides accumulate

To form a reasonable concentration of sulfides, a process is required whereby the sulfide droplets collect together and accumulate to form massive or matrix sulfides. If they do not collect together, then a large volume of rock containing disseminated sulfides may form, but the grade may not be sufficient to form an ore deposit. An example where this may have occurred is at the margins of the Duluth Complex, where many rocks host disseminated sulfides containing 1 to 10 wt percent Ni, with a consequent subeconomic bulk grade of <0.5 wt percent Ni.

In the case of most Ni sulfide deposits, the massive and matrix sulfides occur toward the base of the flows or intrusions that host them or in veins in the immediate footwall. Moreover, in many cases the massive ores are found in association with embayments in the footwall (e.g., massive sulfides of the

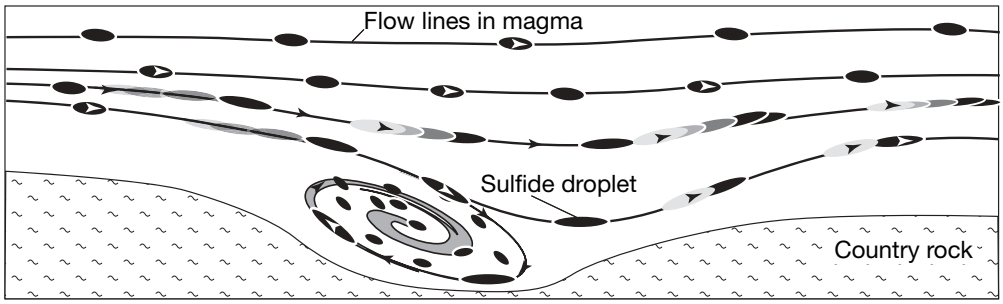


FIG. 21. Cu/Pd vs. Cu for Noril'sk (modified from Barnes and Maier, 1999). Circles = silicate rocks within the intrusions, crosses = lavas above the intrusions, triangles = disseminated and matrix ores. The solid lines represent tie lines between the silicate liquid composition (represented by the lavas) and sulfides formed in equilibrium with the lavas at R factors of 100, 1,000, and 10,000. The solid dots represent the composition of a rock that contains a mixture of 1, 10, or 100 percent sulfides. Most of the Noril'sk sulfides plot in the vicinity of R factors of 1,000 to 10,000. The dashed lines represent models of the silicate liquid composition as sulfide liquid is removed in cotectic proportions. Many of the silicate rocks overlying the sulfide ores plot in this depleted field.

Talnalk intrusions; Fig. 4b). This may be explained if the silicate magma transporting sulfide droplets rises on the downstream side of the embayment, slows, and is therefore no longer capable of carrying the sulfide droplets, which then collect on the lee side of the embayment (Fig. 16e). At Sudbury, the largest Ni sulfide contact ores occur in embayments where the overlying norites of the complex are thickest (Lightfoot et al., 2001). The embayments are thought to represent topographic lows in the crater floor (Golightly, 1994). The accumulation of sulfides is related to the downward migration of dense sulfide liquid along the axis of the embayment and down the flanking walls (Lightfoot et al., 2001).

Another place where sulfide liquid can collect is where the feeder conduit enters an intrusion. When the magma enters the chamber through a narrow feeder it will slow down as it spreads into the chamber and thus may not be capable of carrying the sulfide droplets. The Eastern Deeps deposit and possibly the Ovoid deposit at Voisey's Bay (Fig. 8b, c) are examples of this process (Naldrett et al., 1996b). Other examples are the offset dikes at Sudbury, where the location of orebodies in the dikes correlates with the wider parts of the dike, e.g., the Worthington offset dike (Lightfoot and Farrow, 2002). All of these examples serve to illustrate the important point that structural traps, where the flow velocity of magma was reduced, are important sites for collection of sulfides.

Fractionation of sulfide liquid

Many massive and matrix sulfides have lower metal tenors than associated disseminated sulfide ores (e.g., Cape Smith, Voisey's Bay, Sudbury; Table 3, Fig. 12b, c, f). This can be explained if the disseminated sulfides represent sulfide droplets that did not settle out of the magma and were therefore able to interact with the magma for a longer time, i.e., they interacted with a larger volume of magma than the massive and matrix ores. Thus, the disseminated sulfides had a higher R or N factor and became more enriched in Ni and PGE. Assuming a Pd content of the silicate magma of ~10 ppb at Cape Smith (Barnes and Picard, 1993) and applying equation (5), the disseminated sulfides would require an R factor of 1,000, while the massive and matrix sulfides would require an R factor of 330.

In addition to the metal abundance, metal ratios also vary with sulfide type. In general, the average massive ores have lower Pd/Ir ratios than the disseminated sulfides (Table 3, Fig. 12), and massive and matrix sulfides show a wider range of Ni/Cu and Pd/Ir ratios than disseminated sulfides. This is thought to be the result of crystal fractionation of Fe-rich mss from the sulfide liquid (Fig. 16f; Barnes et al., 1997a). The first phase to crystallize from a base metal sulfide liquid at ~1,199°C is Fe-rich mss (Kullerud et al., 1969). Nickel is moderately incompatible with mss at temperatures greater than 1,150°C (D_{Ni}^{mss} = 0.4–0.6), and Cu is strongly incompatible (D_{Ni}^{mss} ~0.23; Table 4). Palladium and Pt are also incompatible with the mss, whereas Os, Ir, Ru, and Rh are strongly compatible (Table 4). Thus, the sulfides that form from komatiites crystallize into Fe-rich mss enriched in IPGE and the fractionated sulfide liquid becomes rich in Ni, Cu, Pt, and Pd. An example of this is the komatiite-hosted sulfides at Alexo, Ontario, where the massive sulfides (mss cumulate) are richer in IPGE and poorer in Ni than the matrix sulfides (fractionated sulfide liquid; Barnes et al., 1997b). At <1,000°C Ni is moderately compatible with mss (D_{Ni}^{mss} = 1–1.5), and thus in gabbro-hosted sulfides the sulfide liquid forms an mss cumulate rich in IPGE and a Cu-rich liquid rich in Pt and Pd, as noted in the Oktabr'sky deposit at Noril'sk (Barnes et al., 1997a).

For those cases where the data are available, the massive and matrix ores have been divided into those with Pd/Ir ratios less than the disseminated sulfides and those with Pd/Ir ratios greater than disseminated sulfides (Table 3, Fig. 14a-d). Comparison of the two shows that IPGE are enriched in the Fe-rich mss, whereas Cu, Au, Pt, and Ag are strongly depleted, implying very low partition coefficients into Fe-rich mss. Selenium is slightly lower in the Fe-rich mss sulfide, implying that it is slightly incompatible. Cobalt shows a similar behavior to Ni, being slightly enriched in Fe-rich mss sulfides in the gabbro-hosted sulfides and slightly depleted in the komatiite- or picrite-hosted sulfides. The partition coefficient for Co into mss may also be controlled by temperature. Zientek et al. (1994) showed that at Noril'sk-Talnakh, As, Bi Cd, Pb, Sb, Te, and Tl tend to be concentrated in the Cu-rich sulfides. Theriault and Barnes (1998) made a similar observation

for As and Sb at the Duluth Complex, suggesting that As and Sb are not included in mss. At the Cape Smith and Pechenga deposits, which have undergone metamorphism, As and Sb values are erratic, and hence we assume these elements have been mobilized.

Injection into veins

The Cu-rich sulfides are economically significant because they contain high concentrations of the precious metals, Pt, Pd, Ag, and Au. A Cu-rich liquid does not completely solidify until the temperature decreases to below 900°C. In both the case of a komatiite and a gabbroidal host, the silicate rocks would be expected to reach their solidus above this temperature. Thus, the Cu-rich sulfide liquid could have migrated along the contact between the country rock and the now-solid komatiite or mafic intrusions. Moreover, if deformation occurs before the Cu-rich sulfide liquid solidifies, the liquid could migrate into dilatant structures in the footwall (Fig. 16g). In these cases the veins should contain material that represents fractionated sulfide liquid. The vein material at Noril'sk and Cape Smith, which is rich in the elements incompatible with mss (Cu, Pd, Pt, Ag, As, Sb) and depleted in elements compatible with mss (IPGE), probably represents Cu-rich fractionated liquid.

In the case of Sudbury, Cu-rich veins are particularly important, as the meteor impact would have produced large fractures in the crust into which the Cu-rich sulfide liquid could have migrated over long distances (e.g., Li et al., 1983; Naldrett et al., 1999). However, not all authors agree that the Cu-rich sulfide veins at Sudbury represent Cu-rich sulfide liquid. It has been suggested that a contrast in temperature and composition between the Sudbury Igneous Complex and the country rocks triggered the establishment of large hydrothermal cells in the footwall of the complex that resulted in the deposition of the Cu-PGE sulfide veins (e.g., Molnar et al., 1997; Farrow and Watkinson, 1999). Alkali- and halogen-rich fluid inclusions have been found in the sulfides (Jago et al., 1994) and in the minerals associated with the veins (Molnar et al., 1997). Jago et al. (1994) suggested that the magmatic sulfide liquid contained a small amount of halogens and water which originated from the silicate magma. During mss fractionation the halogens and water concentrated into the sulfide liquid and eventually exsolved to form the halogen-rich fluid inclusions now found in the sulfides. This interpretation is supported by the experimental work of Mungall and Brenan (2003), who showed that Cl, Br, and I are incompatible with mss and concentrate in the Cu-rich sulfide liquid. However, Farrow and Watkinson (1999) suggested that the fluids have actually remobilized the metals.

Structural disturbances and metamorphism

The presence of massive sulfides at the base of komatiite flows, or a gabbro sill, represents an incompetent zone with competent silicate rocks on either side of it. When this material is deformed, the deformation will tend to concentrate in the massive sulfides. Thus, the sulfides will deform and flow plastically, but the silicate rocks cannot flow and at the edges of the massive sulfides the silicate rocks will be broken up to form breccia clasts (Figs. 11h, 16h). These clasts could come from either the underlying country rock or the overlying host. At Pechenga (Barnes et al., 2001b), the sulfides in the breccia matrix have slightly lower concentrations of most metals than the massive ore but a slightly higher As content. The reason for this is believed to be the presence of ~20 percent sulfide derived from sedimentary fragments in the breccia. The sedimentary sulfides contain very low metal contents and thus dilute the metal concentrations. The only chalcophile element that is present in the sedimentary rocks at high concentrations is As.

Metamorphism can be important in upgrading the Ni content of the sulfides. It is particularly relevant in the case of the Western Australia komatiite-hosted deposits (Barnes and Hill, 2000).

Ratio Plots: Application to Exploration

Plots that show the ratios of the metals in ores and rocks offer a useful approach to not only understand the petrogenetic relationships but also provide an indication of the potential for the discovery of hidden orebodies. In many exploration programs only Ni, Cu, Pd, and Pt data are available and thus the data cannot be recalculated and expressed as sulfide metal tenors. Even with a limited data set, however, much can be said about the origin of the sulfides based on the variations in Cu/Pd versus Pd. This approach is illustrated for the Noril'sk data (Fig. 20). The initial silicate magma, represented by the basalts (plus symbols, Fig. 20) had approximate mantle ratios for Cu/Pd and contains approximately 10 ppb Pd, indicating that the magma was fertile with respect to Cu and PGE. When a sulfide liquid segregates from a silicate liquid of this composition, the Cu/Pd ratio of the sulfide liquid will depend on the R factor, with low R-factor sulfides having Cu/Pd ratios similar to the silicate liquid, and sulfides with R factors >1,000 having Cu/Pd ratios less than mantle values. Tie lines have been drawn between the composition of the sulfide liquid at R = 100, 1,000, 10,000 and the basalt (Fig. 20). The disseminated sulfide samples from the Talnakh and Kharaelakh intrusions (open triangles, Fig. 20) plot close to the R = 1,000 line and can be modeled as a mixture of basalt and 1 to 30 percent sulfide liquids formed at approximately this R factor (Fig. 20). The samples from the Noril'sk I intrusion (solid triangles) have lower Cu/Pd ratios and plot along the R = 10,000 mixing line, indicating a more dynamic setting. Massive sulfides could also be plotted in this diagram. The fractionation of mss does not change Cu/Pd ratios significantly (because Cu and Pd have similar partition coefficients into mss), and thus it is possible to deduce whether massive sulfide samples formed from depleted or fertile magma and estimate the R factor. However, the amount of sulfides present is not easily estimated from the tie lines because the Pd content of the sulfide fraction may have been changed by mss fractionation, with the Pd content of the mss cumulate being diluted and the Pd content of Cu-rich liquid increased.

Interestingly, many of the rocks from the upper portions of intrusions have Cu/Pd ratios greater than the mantle (open circles) and plot along curves that indicate that sulfides have been removed from the liquid (Figs. 7, 20). In an exploration program this type of signature is useful since it indicates the presence of sulfides stratigraphically below the depleted horizon or upstream from it, and this observation should encourage exploration to focus on targets in these directions. More

specific details on the application of Cu/Pd plots are given in Barnes et al. (1993) and Barnes and Maier (1999).

Plots of Ni/Cu versus Pd/Ir and Ni/Pd versus Cu/Ir can also be very useful in interpreting the relationship between sulfides and the host rocks. This point is illustrated by the flood basalt-associated Oktyabr'sky of Noril'sk-Talnakh, the komatiite-associated deposit at Perseverance, Western Australia, and the Eastern Deeps deposits associated with the Voisey's Bay troctolites. In the Ni/Cu versus Pd/Ir plot (Fig. 22a), the averages of rocks containing disseminated sulfides plot in the field of the host-rock type (open triangle = flood basalt of Noril'sk, open square = high Mg basalt of Voisey's Bay, open circle = komatiite of Perseverance).

The average composition of the massive sulfides plots at lower Pd/Ir ratios and higher Ni/Cu ratios than the disseminated sulfides at Voisey's Bay and Perseverance (solid square vs. open square and solid circle vs. open circle, respectively), possibly because the massive sulfides consist largely of Fe-rich mss cumulates. Inspection of the data in Table 2, plus data from the literature, indicate that this is generally the case; the average of the massive sulfides has a higher Ni/Cu ratio and lower Pd/Ir ratio than the average composition of disseminated sulfides. An exception to this observation is the Oktabr'sky deposit at Noril'sk, where the average massive sulfides have very similar compositions to the disseminated sulfide (Table 2) but have slightly lower Ni/Cu ratios and slightly higher Pd/Ir ratios than the disseminated sulfides (solid triangle vs. open triangle, Fig. 22a). This is probably because the Oktabr'sky massive sulfide crystallized in situ and the Cu-rich fractionated liquid is still part of the deposit.

The massive and matrix sulfides have been divided into those with Pd/Ir > disseminated sulfides and those with Pd/Ir < disseminated sulfides (Table 2). Massive and matrix sulfides with Pd/Ir < disseminated sulfides are Fe rich and plot along the mss accumulation vector (inverted solid triangle, Fig. 22a), while those with Pd/Ir > disseminated sulfide are Cu-rich sulfides and plot along mss removal trends (inverted open triangle, Fig. 22a). In the Ni/Cu versus Pd/Ir plot (Fig. 22a) the effect of sulfide liquid segregation is muted because sulfide liquid does not fractionate Pd from Ir and only slightly fractionates Ni from Cu.

To understand the effect of sulfide liquid separation, the Ni/Pd versus Cu/Ir variations must be examined (Fig. 22b). Removal of sulfide liquid from silicate magma will deplete the magma in PGE more than Cu and Ni (Fig. 12). Any sulfides that form subsequently from this depleted silicate magma will have very high Ni/Pd and Cu/Ir ratios. The Voisey's Bay sulfides appear to be of this type as they plot well above the field of primary magmas (squares, Fig. 22b). The depleted nature of the Voisey's Bay sulfides suggests either that there are some more PGE-rich sulfides at depth or that the magma was produced at a sufficiently low degree of partial melting for some sulfides to have remained in the mantle. The Perseverance and Oktabr'sky sulfides (circles and triangles, respectively) plot in the field of komatiites and flood basalts, respectively, indicating that the magma from which they formed was not depleted in PGE.

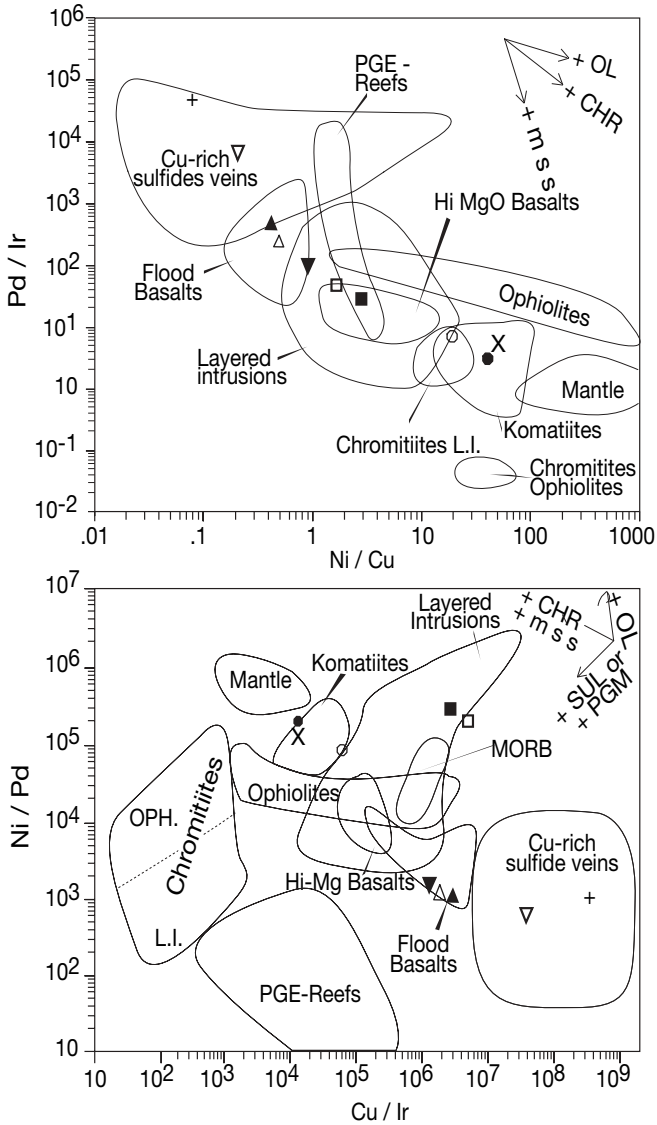


FIG. 22. Ratio plots of (a) Ni/Cu vs. Pd/Ir, and (b) Ni/Pd vs. Cu/Ir (modified after S.J. Barnes et al., 1988) for common rock types. a. The Perseverance sulfides hosted in komatiites (circles) plot in the komatiite field, Voisey's Bay sulfides (squares) plot in the high Mg basalt field, the Noril'sk disseminated and massive sulfides (triangles) plot in the flood basalt field. The Noril'sk Cu-rich sulfides (inverted triangle open) and veins (+) plot in the vein field. In general, massive sulfides (solid symbols) have higher Ni/Cu ratios and lower Pd/Ir ratios than the disseminated sulfides, due to mss accumulation. Cu-rich sulfides have higher Pd/Ir and lower Ni/Cu ratios, due to mss removal. b. The effect of sulfide segregation is visible. Sulfides in equilibrium with magmas that have previously segregated sulfides (such as the Voisey's Bay sulfides; squares) have higher Ni/Pd and Cu/Ir ratios than the primary magmas. In contrast, sulfides such as from Noril'sk formed at high R factors and have similar Ni/Pd and Cu/Ir ratios to those of primary magmas.

Summary and Implications for Exploration

The value of a significant Ni-Cu-PGE discovery can exceed several billion US dollars. Thus, there is an enormous impetus to refine exploration models and develop methods that can be added to the toolbox of exploration geologists. Of key importance in a grassroots setting are criteria that can be used effectively to distinguish terranes with the potential to host significant deposits versus those which do not warrant serious consideration. However, there is a grave danger in excluding terranes. Before the discovery of Voisey's Bay the idea of a

significant Ni sulfide ore deposit associated with an anorthosite suite would have seemed unlikely. Furthermore, if we imagine that Sudbury had not been discovered, the idea of searching for large meteor impact craters to find the world's largest Ni sulfide ore deposit would not seem rational. This is to say that the formation of each Ni mining camp appears to have unique features. Nevertheless, most of the Ni sulfide mining camps and ore deposits show some common features that may be used as guide lines for exploration, as summarized below.

Large volumes of mafic or ultramafic rocks are present. These are normally tholeiitic, picritic, or komatiitic in composition and thought to be derived from a mantle plume. The Sudbury Igneous Complex is an exception in terms of its composition, as it was derived from the crust and therefore has a calc-alkali composition.

The deposits are close to crust-penetrating structures. These faults allow for efficient transport of the magma through crust. Magma must be transferred to the crust with minimal fractionation of olivine or segregation of sulfide liquid. Rifts and province boundaries contain structures of this type. The key coincidence of these structures with mantle-plume events appears to be important in the transportation of primitive magmas.

Sulfur-bearing sediments, in the form of black shales, paragneiss, or evaporites are present in the vicinity of most deposits. The assimilation of these sediments appears to bring about sulfide saturation of the magmas. Rift environments commonly contain sedimentary rocks and offer a source of crustal S that is readily digested along well-bedded stratigraphic horizons that are invaded by the mafic magma.

At the margins of many deposits a zone of sulfide-bearing variable-textured rocks or magmatic breccias are present. These are interpreted as evidence of multiple magma injection and of the transport and redeposition of the sulfides. During transport the sulfide droplets could equilibrate with a large volume of turbulent magma, thus enriching the liquid sulfide in metals.

Magmas that have had sulfide liquid segregated from them are depleted in PGE relative to Ni and Cu. Thus, the rocks overlying Ni sulfide deposits are PGE depleted and have Cu/Pd and Ni/Ir ratios less than mantle values. The same observation should apply to rocks downstream of a Ni sulfide deposit formed in a magma flow.

Massive and matrix sulfides are found at the base of intrusions and flows. In some cases they are in footwall embayments, in others cases they are located where the feeder dike enters the chamber or where a dike widens. All of these sites represent places where the magma flow slowed and thus could not continue to carry the dense sulfide droplets.

In most cases the massive and matrix Ni sulfide ore is zoned with respect to Cu, Au, and PGE concentrations. The Cu-rich zones are enriched in Au, Pd, and Pt, the Cu-poor zones are enriched in Os, Ir, Ru, and Rh. Nickel and Co concentrations are approximately the same in both types of ore. The Cu-rich zones are found either in footwall dikes and veins or overlying the Cu-poor zones. The Cu-rich veins and dikes are present up to >2 km away from some intrusions. The compositional zonation is thought to be the product of mss fractionation from the sulfide liquid.

Massive sulfides are incompetent and stress concentrates at their locations during deformation. Thus, the massive sulfides may be displaced away from their hosts for over 1 km. Therefore, in deformed terranes, the country rock around sulfide-bearing ultramafic or mafic bodies should also be investigated for massive and breccia ore.

The tenor of disseminated sulfides may be significantly upgraded during metamorphism if olivine is destroyed, thereby releasing Ni to the sulfides. Thus, disseminated sulfides in metamorphosed rocks may be exploitable, whereas few disseminated sulfides in fresh rocks are sufficiently rich in Ni to justify mining.

All of these processes have contributed to different extents in different Ni sulfide deposits. What remains remarkable on a global scale is the observation that giant Ni-Cu-PGE sulfide deposits can be produced by mechanisms as varied as meteorite impact, anorthosite magmatism, komatiite flow, and the emplacement of intrusions linked to large igneous provinces. This paper has examined some of the relationships that are common to all of these deposit types, and we hope that future studies will help to advance our understanding of how these deposits form and what can be done to help locate the next major discovery.

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